ECOLOGY OF ACID BROWNWATER STREAMS IN WESTLAND, NEW ZEALAND

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CONTENTS

CHAPTER page

CHAPTER page

CHAPTER page

CHAPTER page

LIST OF APPENDICES

LIST OF TABLES

TABLE page

TABLE page

TABLE page

LIST OF FIGURES

FIGURE page

FIGURE page

FIGURE page

LIST OF PLATES

PLATE page

ABSTRACT

Effects of water chemistry and catchment afforestation on benthic invertebrates were investigated in acid brownwater and circumneutral clearwater streams in Westland, South Island, New Zealand. Annual dissolved organic carbon (DOC) budgets calculated for three North Westland wetland catchments (zero, two and five years post-afforestation) showed that forestry development resulted in a reduction of DOC export by up to 24 % and that recovery of DOC dynamics was linked to the time elapsed since the onset of development. The presence of high DOC concentrations in stream water (up to 41 $g.m^{-3}$) resulted in lowering of pH to about 4.0. These highly acidic waters also contained high concentrations of dissolved aluminium, but only a small proportion (< 80 $mg.m^{-3}$) was in the toxic labile (inorganic) monomeric form.

Surveys of 29 North Westland streams indicated that benthic invertebrate distributions were not affected by pH above about 4.5, but high summer water temperatures in streams whose catchments had been cleared of native forest appeared to limit the distributions of some taxa. Benthic invertebrate communities in two brownwater and two clearwater streams in South Westland monitored for 12 months had similar taxonomic compositions, but overall, densities were 2.4-4.8 times higher at the clearwater sites. Annual production of *Deleatidium* spp. (Ephemeroptera) larvae, the dominant insect in all four South Westland streams, was similar at three of the sites but was 2.7-4.2 times higher at the fourth site where streambed stability was greatest and flow and temperature regimes were least variable.

Studies of epilithon in the South Westland streams indicated that brownwater and clearwater sites had distinctive algal communities and that considerably more abiotically adsorbed (non-cellular) DOC was present on stones in brownwater streams. In addition, microbial conditioning of allochthonous leaf litter was much slower at the brownwater sites, and both leaves and epilithon from these streams appeared to represent low quality food sources for invertebrates. The results of this study suggest that physiological mechanisms are not important in determining the distributions of benthic invertebrates among the Westland streams examined, but that absolute and relative abundances may be affected by the quality or quantity of food, conditions that are directly or indirectly related to low pH.

CHAPTER 1

CONSPECTUS

Brownwater streams and rivers are found in biomes as diverse as the tropical Amazon basin (Janzen, 1974) and subarctic eastern Canada (Moore, 1987a). Many of them originate in peatlands which cover 3 % of the earth's land surface (Kivinen & Parkarinen, 1981; cited in Clymo, 1984) including 150 million ha in Canada, 60 million ha in the United States and 150 million ha in Russia (Gorham *et al.*, 1984). Janzen (1974) found that, as well as flowing from peat swamps, many "blackwater" streams and rivers in South America, Asia and Central Africa also drain sandy, podzolised soils which cover about 4475 million ha in the tropics.

The colour of brown water is caused principally by dissolved organic carbon (DOC) which becomes visible at concentrations greater than about 5 $g.m^{-3}$ (Malcolm, 1985). Indeed, strong relationships between water colour (absorbance) and DOC concentration have been demonstrated by many workers (e.g., Lewis & Canfield, 1977; Grieve, 1985; Moore, 1985; Collier, 1987a,b). Most streams and rivers have DOC concentrations in the range 1-10 $g.m^{-3}$, but they can be much higher in wetlands (Thurman, 1985). McKnight *et al.* (1985) recorded DOC concentrations in the range 24 to 62 $g.m^{-3}$ in Thoreau's Bog, Massachusetts, whereas Thurman (1985) reported a maximum value of 400 $g.m^{-3}$ in Great Heath, Maine, the largest *Sphagnum* bog in the United States.

Composition of DOC

Research into the nature of aquatic DOC developed slowly until the 1970s when its ubiquity and importance in geochemical reactions and water quality was appreciated. A synthesis of early work by Gjessing (1976) has been superseded by the excellent publications of Thurman (1985) and Aiken *et al.* (1985). Unless otherwise stated, all material in this and the following section comes from these two sources.

The operational definition of DOC is organic material which passes through a 0.45 μm filter, an arbitrary yet convenient and repeatable cutoff point along a continuum of organic particle sizes. There are at least twelve major functional groups associated with natural organic matter (e.g., carboxylic, hydroxyl, phenolic) and they play an important role in many of the geochemical reactions associated with DOC (discussed later). Only about 20-25 % of DOC consists of identifiable compounds which include carbohydrates (~10 %), carboxylic acids (~7 %), amino acids (~3 %) and hydrocarbons (~1 %) (Fig. 1.1.). Aquatic carboxylic acids consist primarily of nonvolatile fatty acids whereas carbohydrates are composed mostly of polysaccharides and humic-saccharides.

Hydrophilic acids comprise about 25-30 % of total DOC in most waters (Fig. 1.1.), and are defined functionally as dissolved organic material which is not retained by XAD resin at pH 2. Their composition is not known but some workers speculate that this fraction includes sugar acids such as the uronic, aldonic and polyuronic acids. McKnight *et al.* (1985) suggested that hydrophilic acids include intermediate products in the degradation of organic matter to CO_2 or fulvic acid.

The proportion of DOC which sorbs to XAD resin at pH 2, the so-called humic substances, accounts for around 50 % of total DOC in most streams and rivers (Fig. 1.1.), and up to 90 % in some brown waters. About 90 % of aquatic humic substances are fulvic acids and 10 % are humic acids, although the proportion represented by the former decreases in organically-coloured waters. Separation of fulvic and humic acids is achieved by adjusting humic substance concentrates (> 500 $g.m^{-3}$) to pH 1 at which point humic acids precipitate out and fulvic acids remain in solution.

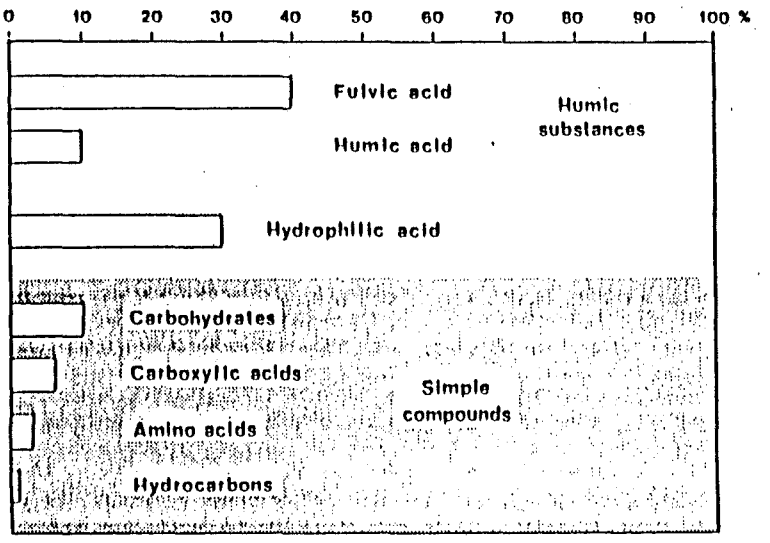


Figure 1.1. Proportions of dissolved organic carbon fractions in an "average" river water sample with 5 $g.m^{-3}$ DOC (from Thurman, 1985).

Visser (1984) found that because aquatic humic acids are coloured more intensely than fulvic acids, they contributed over 30 % of the colour but only 15 % of total dissolved organic matter to lake, swamp, stream and river water samples from Quebec, Canada. Humic acids tend to be larger (molecular weight (mwt) > 2000) than fulvic acids (~800-2000 mwt), and sometimes they are associated with clay minerals or amorphous oxides of aluminium and iron. Meyer (1986) found that over half the DOC in Black Creek and Ogeechee River, Georgia, U.S.A., was of intermediate molecular weight (1000-10000), and similar findings were reported by Moore (1987a) for DOC in Canadian peatland waters.

Sources of DOC

The origin of the DOC present in fresh waters may have several sources. They incude:

1) leaching of plant organic matter directly into the water;
2) leaching of plant organic matter through the soil profile where it is altered chemically and biochemically before entering a stream;
3) leaching of soil fulvic and humic acids (i.e., from soil organic matter) into the water;
4) in-stream biological activity such as algal lysis or excretion by invertebrates;
5) in-stream humification whereby simple reactive compounds are polymerised and condensed into aquatic humic substances.

The relative contributions of these processes undoubtedly varies depending on the source of water and the time of year. Although soil organic matter probably contributes some DOC to streams, leachates from plant material are also believed to be important. During rainfall, organic substances that are leached from living vegetation and decomposing plant litter are flushed into soil interstices. About half this material consists of labile compounds (principally carbohydrates) most of which are oxidised or metabolised rapidly in the upper layers of the soil. The remaining 50 % consists of small, yellow-coloured organic acids comparable to aquatic fulvic acids. They may enter a stream via groundwater, bankflow or by flushing during rainfall events, although some may be metabolised by soil microbes or adsorbed onto mineral particles. The latter process was shown to be important in a New Hampshire podzol where about 90 % of DOC in drainage water was removed in the B horizon, so that DOC concentrations in streams were only 2-3 $g.m^{-3}$ (McDowell & Wood, 1984). Meyer (1986) found higher DOC concentrations in interstitial water of benthic sediments

than in the overlying water column of Ogeechee River, and suggested that leaching of buried particulate organic matter was another potential source of DOC, whereas Naiman *et al.* (1987) implicated groundwater as a major source of DOC in boreal forest, brownwater streams in Quebec, Canada.

In some wetlands, plant leachates may be the dominant sources of DOC, particularly where emergent plants are common. Thus, McKnight *et al.* (1985) concluded that upper layers of *Sphagnum* and humified peat were the major sites of DOC production in Thoreau's Bog. *Sphagnum* may also be an important source of some hydrophilic acids because it contains 10-30 % (dry weight) uronic acid polymers (Clymo, 1984). Mulholland (1981) suggested that, although autochthonous sources (principally filamentous algae) comprised only 4 % of the total organic carbon input to a North Carolina swamp-stream ecosystem, they may have been important sources of DOC for stream heterotrophs in early spring when fresh leaf inputs were low and water temperatures were rising.

Labile organic compounds such as those released as algal exudates or through cell lysis (e.g., amino acids, simple sugars) are thought to be in a constant state of flux in freshwater systems. These labile compounds have "lifetimes" of a few seconds to several hours whereas larger, more complex substances that are resistant to microbial breakdown probably have "lifetimes" of months or longer. Meyer *et al.* (1987) showed that growth rates of planktonic bacteria were greatest on the low molecular weight (< 1000) fraction of DOC from Ogeechee River and lowest on DOC in the molecular weight range 1000 to 10000. These bacteria converted total DOC to biomass with an efficiency of 31 % compared with the 20 % reported by Tranvik & Höfle (1987) for bacteria incubated in clear and brown lake waters.

Properties of brownwater habitats

High concentrations of DOC can impart several physical and chemical characteristics to aquatic ecosystems that are not found in clear (low DOC) waters. Perhaps the most obvious of these is the darkly-stained water which can reduce penetration of photosynthetically available radiation and inhibit production of benthic macrophytes and algae. Janzen (1974) suggested that this may be one reason for low productivity of many tropical, "blackwater" rivers. Edwards & Meyer (1987) detected a negative correlation between DOC concentration and gross primary production in Ogeechee River and implicated absorption of light by humic substances as a factor limiting light penetration. Otto & Svensson (1983) reached the same conclusion after

discovering that only light of longer wavelengths (640 nm) reached the bottom of brownwater streams (0.2 m deep) in southern Sweden. Similarly, Bowling *et al.* (1986) found almost complete extinction of light in the blue waveband (~450 nm) in the first meter of water in highly-coloured lakes in Tasmania, Australia.

Nutrient and trace element limitation may be another reason for low productivity in some coloured waters (Janzen, 1974). However, Edwards & Meyer (1987) discounted this as a reason for low primary production in Ogeechee River where nutrient concentrations were "not unusually low". Verry (1975) calculated nutrient yields from some peatland catchments in Minnesota, U.S.A., and found that, although quite low, annual yields were remarkably similar to those for deciduous and coniferous forest catchments in other parts of North America. Nevertheless, DOC is known to form highly stable complexes with important nutrients and trace elements, and as a result their biological availability can be limited (McKnight, 1981; Stewart & Wetzel, 1981; Anderson & Morel, 1982).

Dissolved humic substances can also regulate the toxicity of some metals by the formation of metallo-organic complexes (Reuter & Perdue, 1977; Hart, 1981). Complexation occurs principally with carboxylic and phenolic functional groups of humic substances (1000-10000 mwt), and rate and degree of complexation depend on many factors including humic substance concentration and origin, ionic strength, temperature and pH (Hart, 1981; Malcolm, 1985; Thurman, 1985). To give one example, Reuter & Perdue (1977) found that at fulvic acid concentrations of 1 $g.m^{-3}$, only 8 % of Cu(II) was complexed, whereas almost 50 % formed complexes at 10 $g.m^{-3}$ fulvic acid.

Waterlogged soils and plant communities of wetlands can bind elements by cation exchange with hydrogen ions which are released into the water column (Thurman, 1985). This, along with the accumulation of organic acids in humic waters inevitably results in low pH. Indeed, organic acids are the main buffers of brown waters in the pH range 3 to 5 (Thurman, 1985). Freedman & Clair (1987) reported pH values of 4.6 to 5.6 for some brownwater streams (5.6-14.1 $g.m^{-3}$ DOC) in Nova Scotia, Canada, but similar coloured streams in Alberta have pH minima of 7.0 (Clifford, 1978; McElhone *et al.*, 1987) because they flow over extensive calcereous deposits (McElhone & Davies, 1983). Clymo (1984) noted that *Sphagnum* bog waters typically have a pH around 4.0, whereas Patrick *et al.* (1979) reported a minimum pH of 3.6 for brownwater streams draining cedar and *Sphagnum* wetlands in the New Jersey Pine Barrens.

High acidity can affect the distribution, density and diversity of aquatic biota at all trophic levels (Dillon *et al.*, 1984 and references therein). Effects on fish populations have been detected when pH declines below 6.0-6.5, and most fish species and many groups of benthic invertebrates are often absent from waters that average pH 4.9 or less (Magnuson *et al.*, 1984). The reasons for depauperate fish and invertebrate faunas in acid waters are not well understood but are thought to include disturbance of ion regulatory mechanisms and calcium metabolism, metal toxicity and changes in the availability and quality of food. Janzen (1974) suggested that the phenolic nature of humic substances may be toxic to aquatic organisms by affecting gaseous exchange through the formation of insoluble protein complexes on respiratory surfaces. Toxicity of phenolics was also implicated by Saber & Dunson (1978) who found high mortalities of brook trout embryos (*Salvelinus fontinalis*) kept in neutralised bog water.

Faunas of brownwater streams and rivers

Although acid brownwater streams and rivers support a wide range of aquatic organisms, they are generally considered to have depauperate faunas compared with unpolluted, circumneutral clearwater habitats. For example, of 70 species of native freshwater fishes recorded from New Jersey, only 16 are known to inhabit brown waters of the Pine Barrens area (Hastings, 1979). Invertebrate faunas of brownwater streams have not been studied widely, but much of the work that has been done suggests that they too are impoverished. An early observation to this effect was made in 1925 by N.Y. Sandwith (cited in Janzen, 1974) when he and his party "took their famous shortcut down the "black" or coffee-coloured, *mosquito-less* rivers past Javita....The return journey was made up the "white" Rio Casiquiare, which connects the Rio Negro with the Orinoco, and is remarkable for the wilderness of its banks and the *blood-thirstyness of its mosquitoes*" (my italics). Jones (1948) studied stony, brownwater and clearwater streams in south Wales and found that the most acidic (pH 4.2-5.8), brownwater site was colonised by only 55 invertebrate taxa whereas 130 were taken from a nearby clearwater stream with circumneutral pH. More recently, Otto & Svensson (1983) surveyed faunas of brownwater streams in southern Sweden and found a positive correlation between water pH and the number of invertebrate species present.

Faunal studies in North America have focussed principally on invertebrate production and trophic pathways in "blackwater" streams and rivers on the coastal plains of Georgia and South Carolina (Benke *et al.*,

1984; Smock *et al.*, 1985; Smock & Roeding, 1986; Wallace *et al.*, 1987). These waterways have predominantly sandy or muddy beds and woody snags often provide the principal stable substrata for invertebrate colonisation. Annual production on snags in these rivers can be very high (up to 67.1 $g.m^{-2}$) and is often dominated by filter feeders and other collector-gatherers which feed mainly on fine particulate organic matter. In contrast, invertebrate faunas are less diverse in slow-flowing, brownwater streams of the New Jersey Pine Barrens where few caddisflies, stoneflies or mayflies were reported by Patrick *et al.* (1979).

To my knowledge, the only other major studies of brownwater stream invertebrate faunas have been carried out in Canada. McDowell & Naiman (1986) investigated the effects of beaver impoundments on benthic invertebrate communities in several brownwater streams (pH 4.8-7.2) of north-eastern Quebec. Non-impounded sites were dominated by Simuliidae, chironomids, scraping mayflies and net-spinning caddisflies. McElhone & Davies (1983) and McElhone *et al.* (1987) studied abundances and microhabitat distribution of Trichoptera in Hartley Creek, Alberta, while Clifford (1978 and references therein) spent over ten years investigating the life histories and general ecology of invertebrates in nearby Bigoray River. The brownwater streams studied by Clifford and McElhone and co-workers both had pH > 7, and in Bigoray River at least 189 insect species were collected including 109 Chironomidae, 39 Coleoptera, 19 Ephemeroptera and 16 Trichoptera. This is more than the 120 insect species collected by Mackay (1969) in four forested, circumneutral clearwater stream sites in Quebec.

New Zealand brownwater streams

In New Zealand, brownwater streams occur predominantly on the west coast of South Island and many drain wetland areas known as pakihis - "a swampy acidic barren type of land" (Hulme, 1984). Until recently, very little work had been done on the chemistry or biology of these streams, but the last few years have seen an acceleration of research. Spectral properties of a range of West Coast brownwater and clearwater sites were investigated by Collier (1987a,b; Appendices I and II), and Moore (in press) included a pakihi stream in his study of absorbance characteristics of several North Westland waters. Moore (1987b) included the same stream in a concurrent study of DOC fluxes in wetland and afforested catchments in North Westland.

Ecological studies of West Coast brownwater streams have been concerned largely with the distribution of fish (McDowell *et al.*, 1977; Main *et al.*, 1985) and the annual migrations of commercially important whitebait species (McDowell & Eldon, 1980). Main *et al.* (1985) observed that koaro (*Galaxias brevipinnis*) apparently avoided brownwater tributaries but that banded kokopu (*G. fasciatus*) was common in such waters. The hypothesis that the former species is sensitive to low pH was confirmed in subsequent experimental and field work in which Main (1987) also investigated diets of several galaxiid species (see also Main & Winterbourn, 1987 and Main & Lyon, in press).

The only published studies of benthic invertebrate ecology in New Zealand brownwater streams are those of Graesser (in press), Winterbourn *et al.* (in press) and Winterbourn & Collier (1987). Graesser (in press) investigated invertebrate drift in three brownwater streams in South Westland and found that drift densities were low (< 0.01 % of benthic invertebrate numbers) but increased as stream discharge dropped. Winterbourn *et al.* (in press; Appendix III) reviewed ecological studies being carried out in seven small streams with pH and DOC ranges of 4.3-8.0 and 0.3-16.3 $g.m^{-3}$, respectively. They could not distinguish consistent temporal or spatial patterns in community structure or productivity among streams, and concluded that this was because of the highly variable and unpredictable discharge regimes that characterised most sites. Winterbourn & Collier (1987; Appendix IV) conducted a survey of water chemistry and benthic invertebrate distribution in a large number of West Coast streams and rivers. They found that species composition and taxonomic richness of invertebrate communities was not correlated with water pH (range 3.5-8.1) or any other measured chemical parameter (DOC, conductivity, alkalinity or total reactive aluminium), and that many taxa occurred over a very wide pH range down to a lower limit of about pH 4.5. Furthermore, sites in close proximity tended to have similar faunas suggesting that the pool of available colonists rather than immediate pysicochemical factors was the prime determinant of species richness at a particular locality.

Rationale for the present study

The effects of low pH on aquatic ecosystems have been of increasing concern to biologists in recent years with the acidification of many Northern Hemisphere surface waters by acid rain. Research in this field has resulted in an ever-expanding literature (see Haines, 1981 and Dillon *et al.*, 1984 for reviews), and has demonstrated pH-related changes in benthic communities at all trophic levels. However, the causes of all changes have not been resolved satisfactorily; some workers have suggested that physiological mechanisms are most important (e.g., Hall *et al.*, 1980; Allard & Moreau, 1987; Ormerod *et al.*, 1987), and others that changes in food or energy supplies may be the main causal factors (Sutcliffe & Carrick, 1973; Otto & Svensson, 1983). Concern has been expressed also about the deleterious effects of elevated aluminium concentrations in acidified waters (Baker & Schofield, 1982; Odonnell *et al.*, 1984), and Hall *et al.* (1987) suggested that fluctuating aluminium concentrations at pHs that are not normally detrimental may be primarily responsible for altering the biology of poorly-buffered, aquatic ecosystems.

Considering the intensity of interest in acid streams, and the cosmopolitan distribution of naturally acidic waters, it is surprising that few workers have examined the effects of low pH on benthic communities in brownwater streams. Exceptions are Jones (1948) in south Wales, Otto & Svensson (1983) in southern Sweden, and Mackay & Kersey (1985) who included some brownwater sites in their study of leaf breakdown and invertebrate communities in acidified Canadian streams. However, the streams studied by all these workers are in areas influenced by acid precipitation and it is unclear to what extent this was affecting the sites.

Acid rain is not a problem in New Zealand where rainwater pH is around 5.6 and sulphur deposition is about forty times less than on the worst affected areas of Europe (Holden & Clarkson, 1986). The numerous acid brownwater streams in Westland, uninfluenced by acid precipitation, provide an excellent opportunity to investigate relationships between physicochemical factors (particularly pH, DOC and aluminium), and the distribution, population dynamics and trophic resources of benthic invertebrates. Also, because about half of recent pine forest plantings in Westland have been on pakihis (N.Z. Forest Service, 1984), the effects of afforestation on sources of acidity (principally DOC) and benthic invertebrates are of interest. Northern Hemisphere work has indicated that afforestation may increase streamwater acidity through the removal of soil base cations which are exported from the catchment after clear-felling, and

through trees collecting acidic, airborne pollutants which eventually are transported to drainage waters. The relative contribution of these processes remains a moot point, however (e.g., Rosenqvist, 1978; Harriman & Morrison, 1982; Ormerod & Edwards, 1985) and was the subject of a recent paper by Flower *et al.* (1987) who concluded that acid deposition was the most probable cause of acidification in some Scottish lakes draining afforested catchments.

Specific questions asked in the present study were:

1) What are the sources and fluxes of DOC in pakihi streams and what effect does afforestation have on them?
2) What chemical parameters are characteristic of brownwater streams?
3) What effects do these parameters have on the distribution of benthic invertebrates in localised areas and how is this influenced by afforestation?
4) Are invertebrate communities less productive in undisturbed brownwater streams than at circumneutral clearwater sites?
5) Is the quality and quantity of available food different in brownwater and clearwater streams?
6) How does ecosystem structure and function in acidic Westland streams differ from that in Northern Hemisphere streams acidified by acid rain?

These questions are addressed in the following chapters. Chapter 3 presents DOC budgets calculated for three pakihi streams, two of which had been developed for forestry. This is followed by an investigation of the inter-relationships between physicochemical parameters at a range of stream sites (brownwater or clearwater, developed for forestry or undeveloped) in North and South Westland. Benthic invertebrate distributions in the same North Westland streams are examined in Chapter 5. Because Winterbourn & Collier (1987) found that invertebrate community composition was influenced by geographic factors, this part of the study was limited to stream communities within a confined locality. Chapter 6 describes population dynamics of benthic invertebrates in two brownwater and two clearwater streams in South Westland, and presents annual production estimates for *Deleatidium* (Ephemeroptera), the most abundant insect at the four sites. The gut contents of selected invertebrate taxa are also considered in this chapter. More intensive research into the nature of food resources available to benthic invertebrates in these streams is presented in Chapters 7 and 8. The former considers the nature of epilithic communities and presents results of feeding experiments with *Deleatidium* larvae. Chapter 8 describes

the relative contributions of microflora and invertebrates to allochthonous leaf litter breakdown in four South Westland streams and discusses the palatability of leaves from different streams to a large-particle detritivore. Major findings are synthesised in Chapter 9 and are contrasted with results obtained in Northern Hemisphere studies of anthropogenically acidified streams. Finally, six appendices present the results of several published and unpublished studies including collaborative work which complement the thesis research.

CHAPTER 2

STUDY AREA

2.1. THE WESTLAND REGION

2.1.1. Physical Description

Westland is a narrow strip of land extending for 400 km down the west coast of South Island, New Zealand (Fig. 2.1.). It is divided conveniently into southern and northern regions by Taramakau River which bisects Westland 16 km south of Greymouth.

Two powerful processes have moulded the present day landscape of the area (Wardle, 1979):

1) movements of the earth's crust along the Alpine Fault;
2) erosion and deposition by glaciers and rivers.

The Alpine Fault runs approximately parallel to the coast and is visible as a sharp dip in the ranges which then merge into low saddles or alluvial fans (Gibbs *et al.*, 1950). Crustal movements have displaced rock strata horizontally by 450 km and caused vertical uplift of rocks on both sides of the fault by about 18000 m (Wardle, 1979). This vertical movement has formed the steep outer ranges of the Southern Alps which dominate the region in the east.

Erosion has almost kept pace with uplift and has limited the maximum height of the Alps to 3764 m above sea level (asl). Extensive glaciations during the Quaternary Era were the most powerful erosive force, depositing spoil on the lowlands in the form of huge moraines (Wardle, 1979). Deposition during glacial advances alternated with interglacial fluvial activity and has resulted in a lowland landscape of hills and terraces with numerous lakes formed in depressions or behind morainic dams. North of Greymouth (Fig. 2.1.), some high ranges (most notably the Paparoas) extend almost to the coast and a number of fluvio-glacial terrace systems have formed inland of these (N.Z. Soil Bureau, 1968).

Glaciers currently are confined to the mountains and feed the head waters of some of the large rivers which traverse the lowlands through broad flood-plains. In many of the rivers, channel velocities are high and suspended sediment yields per annum are about ten times greater than world average rates for mountainous areas (Griffiths, 1979). Along the coast, truncated or jutting glacial moraine headlands, broad beaches and coastal lagoons are typical features.

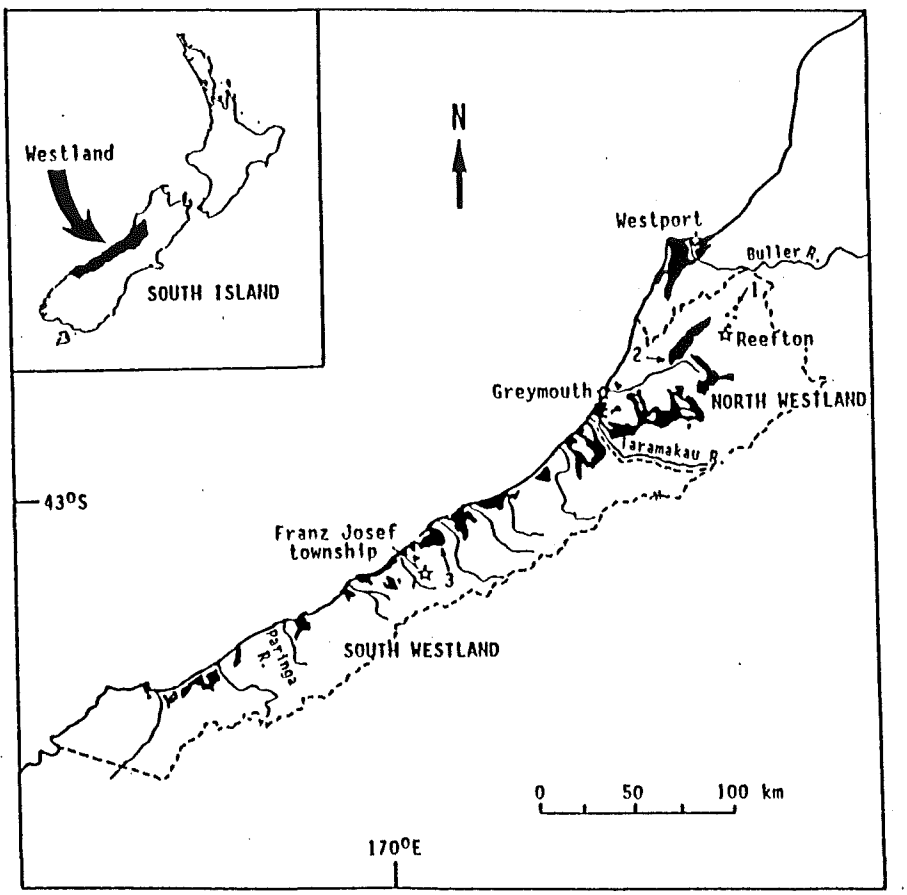


Figure 2.1. The Westland study region. Shaded areas represent pakihis. 1, Larry River pakihi; 2, Craigieburn pakihi; 3, Okarito pakihi. (Adapted from N.Z. Town & Country Planning Branch, 1959).

2.1.2. Geology

The Southern Alps are composed mainly of schist which grades into greywacke (hardened sandstone) and argillite (Warren, 1967). These rocks were formed from strongly indurated and metamorphosed sedimentary material laid down mostly in the Permian and Triassic periods, and were uplifted sometime in the Mesozoic Era. West of the Alpine Fault and north of Greymouth, mountain ranges are formed from Tertiary sandstones and limestones, Paleozoic granites and gneiss, and Precambrian greywackes (N.Z. Soil Bureau, 1968).

On the southern lowlands, bedrock is composed largely of granite and greywacke, but most of this has been buried under recent (14000 years old) glacial outwash gravel and deposits of till (Warren, 1967; Wardle, 1979). Early Pleistocene glaciations in North Westland deposited sediments of coarse, weathered conglomerate (Old Man gravels) which now form terraces around 300-600 m higher than adjacent valley floors.

2.1.3. Climate

The climate of Westland is humid and mild, and is characterised by high annual rainfall which generally increases from north to south and from the coast towards the axial range (N.Z. Town & Country Planning Branch, 1959). In South Westland, annual rainfall is about 350 cm on the coast, but increases to around 500 cm at the foot of the ranges and probably reaches 1000 cm in places amongst them (Wardle, 1979). Highest rainfall in North Westland occurs on the Paparoa Range (up to 500 cm p.a.), but in the rest of the northern region annual rainfall averages less than 375 cm (N.Z. Town & Country Planning Branch, 1959). Rain often occurs as intense falls which are distributed quite evenly throughout the year, although spring and summer are generally the wettest seasons.

Lowland temperatures are relatively mild, although severe winter frosts are experienced in some valleys. The average annual temperature for coastal regions is around 12^{o}C, but temperatures are lower in the high country and permanent snow cover can occur down to 1500 m (N.Z. Town & Country Planning Branch, 1959; Wardle, 1979). Average relative humidity ranges from 79 % to 86 % and is highest in winter. The number of sunshine hours per annum averages 1840 at Hokitika (35 km south of Greymouth) with maximum daylength of 15 hours in summer and the

minimum, 9 hours in winter.

2.1.4. Soils

High rainfall has contributed to severe leaching of most Westland soils and podzolisation is often well advanced. Podzols are characterised by thick surface horizons of mor humus (a fibrous blanket of organic matter low in nutrients), subsurface bleaching, and subsoil accumulations of iron and humus (N.Z. Soil Bureau, 1968).

Steepland soils occupy over 80 % of the region. They are mostly steepland podzols and podzolised yellow-brown earths (Otira-Wakamaramara soils) and gley podzols (McKerrow soils). The former are found on steep to very steep slopes from near the coast to the main axial range, whereas McKerrow soils occur higher in the mountains (N.Z. Soil Bureau, 1968).

Most terrace soils south of Westport are intensely-leached gley podzols (Okarito soils) which are often waterlogged because of poor structure and impervious subsoil pans (N.Z. Soil Bureau, 1968). Some terraces exhibit a mosaic of soil types with widely different profiles, fertility and drainage characteristics (Chavasse, 1962). The matrix includes acid bogs with peaty soils on silts, sand or gravel (Kini soils) and on undulating and rolling surfaces, Waiuta soils which have thin, loamy topsoils and subsoils resting on thin iron pans.

Unpodzolised yellow-brown earths (Ahaura and Arahura soils) have developed on some terrace and hilly areas where drainage is sufficient to allow decomposition of surface organic matter (N.Z. Soil Bureau, 1968). Recent soils (Hokitika-Ikamatua series) and gley-recent intergrades (Harihari-Karangarua soils) are distributed widely on low terraces and flood-plains of the major rivers. The latter are imperfectly- to poorly-drained whereas recent soils are free-draining (N.Z. Soil Bureau, 1968).

2.1.5. Vegetation

The vegetation of Westland is characterised by a distinct succession of forest types from river valley to steepland slopes (Chavasse, 1962). The upper limit of forest and scrub is about 900 m asl in the south and 1350 m in the north. Above these altitudes, subalpine scrub and tussock grassland

occur to the permanent snowline (≥ 1500 m asl). The tract of land between the Taramakau River and Paringa River (Fig. 2.1.) is covered mostly by podocarp-broadleaf forest, but elsewhere forests are mainly mixed beech and beech-podocarp (N.Z. Soil Bureau, 1968).

Steepland and hill forests of the podocarp-broadleaf type consist mostly of rata (*Metrosideros umbellata*), rimu (*Dacrydium cupressinum*) and miro (*Prumnopitys ferruginea*) with kamahi (*Weinmannia racemosa*) as the main sub-canopy tree (Chavasse, 1962). Flat or gently-rolling terrace country supports dense rimu forest with an admixture of miro and kahikatea (*Dacrycarpus dacrydioides*). Terrace forests may also contain silver pine (*Lagrostrobos colensoi*), totara (*Podocarpus totara*) and kaikawaka (*Libocedrus bidwillii*), and have understories which include quintinia (*Quintinia acutifolia*) and kamahi. Well-drained flood-plains are typically colonised by totara and matai (*Prumnopitys taxifolia*) with kahikatea present on alluvium or wetter flood-plains (Chavasse, 1962). In North Westland and south of the Paringa River, similar types of forest are found, but superimposed on them are the migration patterns of four incoming beech species (Holloway, 1954). Red beech (*Nothofagus fusca*), black beech (*N. solandri* var. *solandri*) and silver beech (*N. menziesii*) are common below 600 m asl, and mountain beech (*N. solandri* var. *cliffortioides*) occurs at higher altitudes.

Many Westland terraces have wetland areas (known locally as pakihis) where forest does not grow. Typically, these are colonised by ferns (*Gleichenia* spp.), sedges (*Baumea* spp.), restiads (mainly *Empodisma minus*), rushes (*Juncus* spp.), wire rush (*Calorophus minor*) and manuka (*Leptospermum scoparium*) (Wardle, 1979; N.Z. Soil Bureau, 1968; Mew, 1983).

2.1.6. Westland Pakihis

Technically, pakihis are classified as soligenous plaudification bogs (blanket bogs on flat or sloping surfaces) belonging to the oligotrophic series (Cranwell, 1953; cited in Rigg, 1962). There are about 300000 ha of pakihi land on the west coast of South Island (see Fig. 2.1.), and in North Westland it comprises 19 % of the total land area (Washbourn, 1972; Jackson, 1987). Most pakihis occur on terrace systems composed of glacial and post-glacial outwash materials where annual rainfall exceeds 220 cm. Although soils under pakihi land have a diverse range of physical characteristics, all have four features in common (Mew, 1983). Pakihi soils are extremely acid (pH

usually < 4.5 in upper horizons), naturally infertile, have relatively impermeable subsoils and are saturated with water for a substantial part of the year.

Most large pakihis contain buried timber and as a result some workers (e.g., Holloway, 1954) believe that they were covered in forest (mainly rimu and silver pine) in pre-European times. Conversion to pakihi could have been induced by logging, fire, changes in the physical and chemical characteristics of the soil or regional climatic variations (Mew, 1983). Over the last few centuries, however, forests appear to have been re-invading some pakihis, and in South Westland zones of succession from pakihi to manuka to silver pine and finally to rimu can be distinguished (Holloway, 1954). Mew (1983) concluded that localised variations in water table levels best explain the present distribution pattern of pakihi and forest in South Westland.

Recolonisation of pakihis by forest has largely been halted by the activities of man who has logged and repeatedly burnt many terrace areas so that extensive "induced pakihis" have been formed. Under forest cover, water drains laterally through the litter and A_1 horizons of Okarito soils, but loss of litter after milling has reduced lateral drainage and surface aeration permitting only pakihi vegetation to become established (N.Z. Soil Bureau, 1968). The first burnings were probably carried out on a small scale by Maoris and it was suggested by Wardle (1979) that the pakihis inland from Okarito were first cleared by Maori eeling parties heading for Lakes Wahapo and Mapourika (Fig. 2.3.). In the early years of European colonisation, some pakihis were disturbed by the sinking of gold mine shafts, the digging of sluicing channels and the formation of dams (Rigg, 1962). Where this disrupted impervious subsoil pans, free drainage resulted and many introduced plants now occur at the expense of endemic species.

Early attempts to reclaim pakihis for forestry and pastoral farming were unsuccessful because of poor drainage and natural infertility. Pakihi soils are typically low in phosphorous, calcium, magnesium, potassium, copper, cobalt and molybdenum, and have high carbon:nitrogen ratios (Washbourn, 1972). However, trials on the Buller pakihis near Westport have shown that good pasture growth can result within one year on some pakihi soils which have received adequate top-dressings of lime, superphosphate and essential trace elements (Walton, 1971). Establishing pasture on pakihis can be expensive, and many farmers content themselves with burning the vegetation once a year so that stock can feed on the young regrowth (Rigg, 1962).

Trials on the Craigieburn pakihi, south of Reefton, have shown that forestry may be the most viable commercial use for pakihi land (Washbourn, 1972). Promising results were achieved with three conifer species (*Pinus radiata*, *P. muricata* and *P. contorta*) in areas where drainage was improved and fertilisers applied. About 50 % of recent (~1983) exotic forest plantings in Westland have been on pakihi land, much of which was v-bladed (N.Z. Forest Service, 1984). The v-blading technique draws its name from the shape of the tractor blade which mounds earth up in parallel rows at right angles to stream channels thereby facilitating drainage. V-blading typically removes 2 m wide strips of soil to a depth of about 0.4 m and rolls it out to create mounds about 0.5 m high (Jackson, 1987). Parallel runs of the v-blade are made about 8 m apart and are separated by 2 m strips of undisturbed pakihi soil.

2.2. NORTH WESTLAND SITES

2.2.1. Larry River and Craigieburn Pakihi Streams

Faunal and chemical surveys were made at twenty-nine stream and river sites on or around the Larry River and Craigieburn terraces (Fig. 2.2.; see Chapters 4 and 5). Pakihi land on both terraces has been developed for forestry to varying degrees (mostly by v-blading and planting with pines; see Table 2.1.), and on the Craigieburn terrace, undisturbed brownwater and clearwater streams are found in close proximity.

Rainfall is high (200-381 cm p.a.) and has contributed to the development of mature podzols (Okarito series), although on the Larry River pakihi, Kini soils also occur (Washbourn, 1972; Ross *et al.*, 1977). Beech-podocarp forest colonised the terraces in pre-European times, but logging and burning has induced the establishment of typical pakihi vegetation. In addition to the species listed in Section 2.1.5., gahnia (*Gahnia setifolia*), bracken (*Pteridium aquilinum*), ring fern (*Paesia scaberula*) and *Sphagnum* moss are also common.

The Craigieburn pakihi comprises 7280 ha of gently-sloping terrace (183-335 m asl) on the inland flanks of the Paparoa Range (Washbourn, 1972) (Fig. 2.2.). Development of the area for forestry began in 1953, and since then at least 15 species of trees (mostly *Pinus* spp.) have been planted using a variety of land preparation techniques and fertiliser applications (see Washbourn (1972) for details of initial trials). Most development took place in 1977-78 and 1980-82, and the most recent plantings were in 1986. Some areas of undeveloped pakihi and undisturbed native forest remain, although these are mostly on the outer flanks of the terrace system.

Twenty-two stream sites on and around the Craigieburn terrace were sampled (Fig. 2.2.; Table 2.1.), and all but seven (Sites 1, 4, 5, 6, 7, 21 and 23) were associated with Craigieburn Creek which forms the main drainage network. Sites 9, 12 and 20 were all clearwater streams originating in the surrounding forested hills, whereas Sites 2, 5, 8, 15, 16, 17, 19 and 23 were small, brownwater streams surrounded by undeveloped pakihi or native forest on Okarito soils. Four sites (1, 3, 21 and 22) were on downstream reaches of large streams or rivers draining the Craigieburn terraces, and had some catchment development upstream of the sampling site. All streams run in a southerly direction and eventually flow into Grey River.

The Larry River terrace sequence is situated 14 km north of Reefton

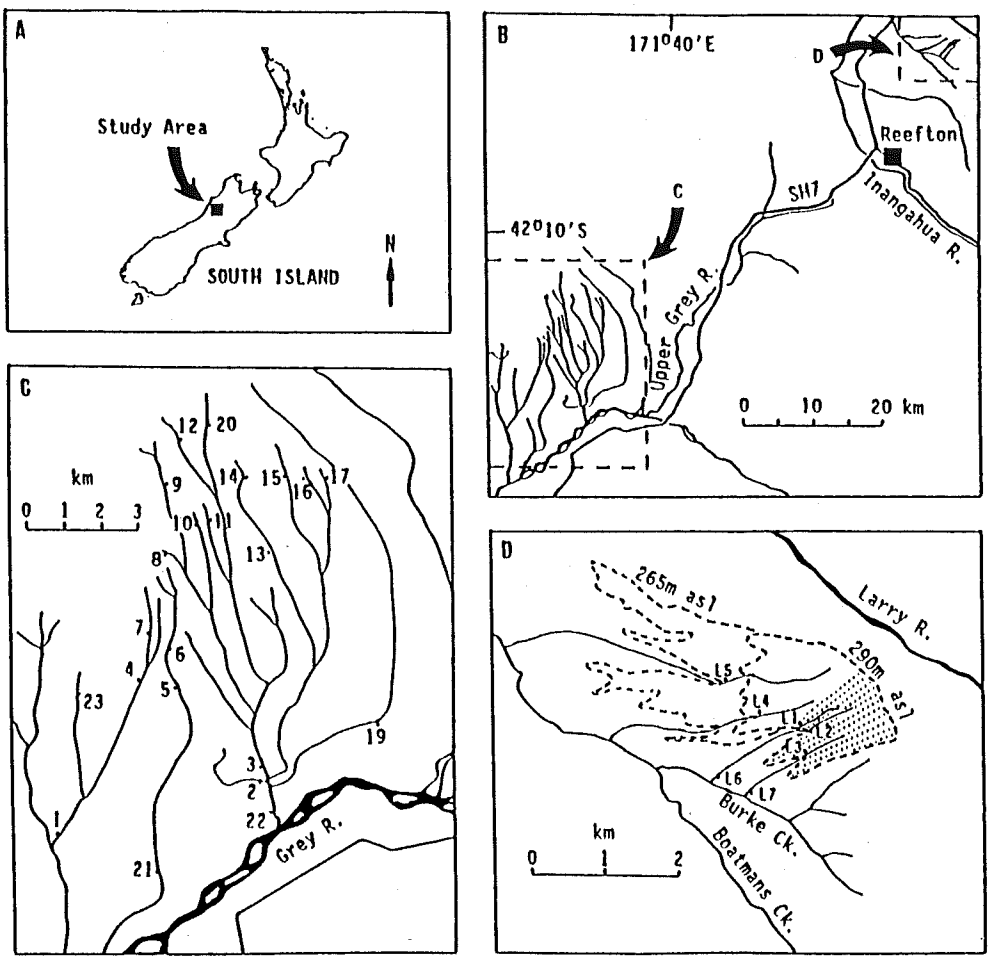


Figure 2.2. Stream survey sites on the Craigieburn and Larry River terraces. A & B, locations of the study areas in North Westland; C, Craigieburn sites; D, Larry River sites. In D, broken lines delineate the two upper levels of the Larry River terrace sequence, and the stippled area indicates the three experimental catchments, L1, L2 and L3. Grid references of all sites are given in Table 2.1.

Table 2.1. Locations and physical characteristics of the 29 North Westland survey sites. Stability was assessed using the streambed component of the Pfankuch (1975) method which gives lower scores to more stable sites. Date of catchment development (v-blading) is given where applicable, and sites have been ranked (1-5) according to their degree of development beginning with undisturbed sites in beech-podocarp forest. Site 18 was not included in the study because samples collected in November were lost.

Site	Map ref. NZMS 1	Channel width (m)	Pfankuch streambed stability score	Date of catchment development	Rank order of development	Adjacent vegetation type
1	S45 033073	5.0	30	*	1	forest
2	S45 086088	4.5	29	-	1	forest
3	S45 085097	15.0	44	*	1	forest, scrub
4	S38 045110	4.0	34	1976 *	3	*Pinus radiata*, scrub
5	S38 064118	3.5	22	*	1	forest
6	S38 063126	3.0	36	1986	5	*P. radiata*
7	S38 057134	2.5	30	1985	5	*P. radiata*
8	S38 063155	2.5	22	-	2	pakihi
9	S38 065163	4.5	43	-	1	forest
10	S38 073156	1.2	25	1980-81	4	*P. radiata*
11	S38 076157	3.0	29	1980-81	4	*P. radiata*
12	S38 072177	3.5	40	-	1	forest
13	S38 091156	2.5	36	1980-81	4	*P. radiata*, *Pseudotsuga* sp.
14	S38 091164	3.0	35	1981-82	4	*P. radiata*
15	S38 096164	4.5	35	-	1	forest
16	S38 104164	2.5	32	-	1	forest
17	S38 108164	2.0	33	-	2	pakihi
19	S38 120198	6.5	22	-	1	forest
20	S38 077178	3.5	40	-	1	forest
21	S45 063063	10.0	30	*	2	scrub and pasture
22	S45 090081	24.0	44	*	2	scrub and pasture
23	S45 038108	3.5	23	-	1	forest
L1	S38 377383	1.7	51	1981-82	4	*P. radiata*
L2	S38 377381	1.0	26	-	2	pakihi
L3	S38 377377	1.0	55	1984-85	5	*P. radiata*
L4	S38 370388	1.4	56	1982-83	4	*P. radiata*
L5	S38 363393	1.2	23	1980-81	4	*P. radiata*
L6	S38 367374	1.3	37	*	1	forest
L7	S38 370373	1.9	38	*	1	forest

*, some catchment development upstream of sampling site.
-, no catchment development upstream.

(Fig. 2.2.), and comprises seven adjacent levels up to 290 m asl (Ross *et al.*, 1977). V-blading and planting with pines began in 1980-81 and now most of the upper terraces have been developed. Seven sites on streams draining the Larry River pakihi were sampled in the survey (Table 2.1.), all streams flowing in a south-westerly direction into Boatmans Creek or its tributary, Burke Creek. Sites L1-L5 flowed across the two upper terraces, whereas the other two sites were on downstream reaches of terrace streams after they had flowed for several hundred meters through beech-podocarp forest.

2.2.2. Larry River Experimental Catchments

Three adjacent catchments (L1, L2 and L3; Plate 2.1.) on the upper level of the Larry River terrace sequence were monitored continuously between April 1983 and April 1988 by Forest Research Institute (FRI), Ministry of Forestry. This program was designed primarily to assess the effects of v-blading on catchment hydrology. I investigated sources and fluxes of DOC carried by streams draining these catchments from August 1986 to July 1987 (see Chapter 3).

Each catchment is roughly rectangular (approximately 800 m long by 150 m wide) and has a gradient of about 1^{o} (Jackson, 1987). L2 is the largest catchment (11.60 ha) and is undeveloped pakihi which was last burnt about 40 years ago. The dominant canopy species is manuka (4-6 m high) which shelters a ground cover of *Sphagnum* moss, bracken and ferns. Water moves laterally at a slow rate and eventually forms sluggish, tortuous streams which frequently disappear beneath the surface vegetation (Jackson, 1987).

At the head of catchment L1 is 3.2 ha of undeveloped manuka forest (see Fig. 3.1.), but the lower 6.8 ha was crushed and burnt in 1981, and in 1982 the catchment was v-bladed and planted with pines. By 1986, the pines were 3-5 m tall and scrub (mostly bracken) had regenerated to a height of 0.5-1.0 m (Jackson, 1987). The v-blade tracks have remained bare but mosses and some rushes have invaded the stream channel. L3 is the smallest (9.87 ha) and more recently developed catchment. Its vegetation was crushed in October 1984, burnt in February 1985, and 2 months later the site was v-bladed. Pines were planted on the mounds in July 1985.

Plate 2.1. Streams draining catchments L2 (upper photo), L1 (middle) and L3 (lower) in Larry River Experimental Area, north of Reefton. L2 was the control catchment (mostly manuka) whereas L1 and L3 were developed by v-blading and planted with pines in 1982 and 1985, respectively.

2.3. SOUTH WESTLAND SITES

2.3.1. Introduction

Five streams included in the West Coast survey of Winterbourn & Collier (1987) were selected for intensive study to obtain quantitative data on faunal and chemical dynamics of brownwater and clearwater streams. These sites were between Franz Josef glacier and Lake Wahapo, a linear distance of 22 km (Fig. 2.3.), and comprised two darkly-stained brownwater, one moderately-stained brownwater and two clearwater sites. Locations and some physical characteristics of sampling reaches in the five South Westland streams are given in Table 2.2.

2.3.2. Brownwater Sites

Steep Creek and Suspect Stream (Plate 2.2.) originate in a lowlying area of pakihi adjacent to the Okarito road. Both streams are darkly-stained, have fairly narrow channels (mean width ~2.4 m), low gradients ($\leq 3^{o}$) and similar streambed stabilities (Table 2.2.). They flow for about 1 km through mainly podocarp forest and eventually enter the Okarito River. Silver pine was cleared from this area at the end of the nineteenth century and again some 50 years later, but since then there has been no disturbance (Stevens, 1968). The moderately-stained brownwater stream is Mapourika Creek. The widest and steepest of the five sites, it flows for about 1 km before entering Lake Mapourika (Table 2.2.). Adjacent soils belong to the free-draining Hokitika-Ikamatua series and contrast with soils in the headwaters of Steep Creek and Suspect Stream which are Okarito gley podzols (N.Z. Soil Bureau, 1968).

Riparian vegetation alongside Suspect Stream (mainly manuka and juvenile podocarps) and Mapourika Creek formed a dense canopy over the sampling reaches. Steep-sided valley walls (slope ~23^{o}) meant that the section of stream bed sampled in Steep Creek received direct sunlight only in the mid to late afternoon. Riparian vegetation alongside Steep Creek and Mapourika Creek was composed primarily of rimu and kamahi with crown fern (*Blechnum discolor*) and tree fern (*Cyathea smithii*) common close to the stream edge. Little allochthonous leaf litter was trapped in the stream channels at any brownwater site, although large amounts of woody debris in

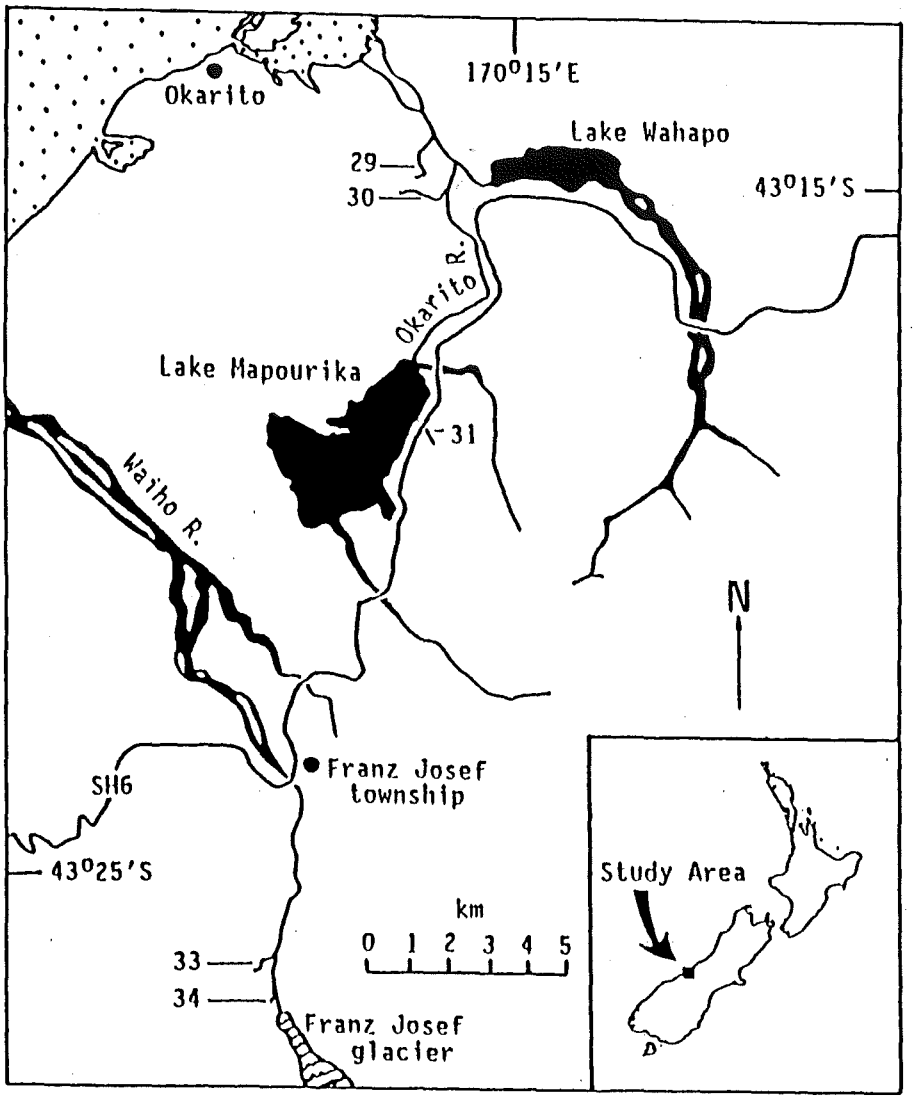


Figure 2.3. Locations of the five South Westland study sites. 29, Suspect Stream; 30, Steep Creek; 31, Mapourika Creek; 33, Toilet Stream; 34, Hidden Creek. Site numbers correspond to those used in Winterbourn & Collier (1987; Appendix IV).

Steep Creek formed several log jams which periodically trapped leaf material. Mosses were present in all three brownwater streams, and in Steep Creek, liverworts and patches of the red alga *Batrachospermum* sp. were seen.

Fish, mostly *Galaxias* spp. but also some long-finned eels (*Anguilla dieffenbachii*), were present in all the brownwater streams studied (M.R. Main, North Canterbury Catchment Board, Christchurch; pers. comm.). Redfinned bullies (*Gobiomorphus huttoni*) were found only in Mapourika Creek.

2.3.3. Clearwater Sites

Toilet Stream and Hidden Creek (Plate 2.3.) are tributaries of Waiho River in the Franz Josef glacier valley (Fig. 2.3.). They had the most stable (Hidden Creek) and one of the most unstable (Toilet Stream) stream beds of the five South Westland sites, although both sampling reaches had similar channel slopes and widths (Table 2.2.).

Hidden Creek emanates from a spring on a rocky, bush-clad hillside (slope 20-31°) and emerges onto an open terrace of fluvio-glacial alluvium about 25 m from its source. The sampling reach was located on this terrace where the stream channel was exposed to direct sunlight for much of the day. In contrast, Toilet Stream is fed by runoff from steep-sided valley walls and flows for approximately 750 m through dense scrub which shades the stream channel. Vegetation alongside both clearwater streams consisted mainly of wineberry (*Aristotelia serrata*), tutu (*Coriaria arborea*), pate (*Schefflera digitata*), mountain akeake (*Olearia avicenniaefolia*) and crown fern. Large quantities of leaves accumulated in the stream channel in Hidden Creek, and these appeared to be retained for relatively long periods, presumably because of the fairly stable flow regime. However, comparatively little allochthonous leaf material was seen in Toilet Stream during the study, although aquatic mosses were more common there.

Soils around Hidden Creek and Toilet Stream are poorly-developed and comprise a thin (2-3 cm) layer of mor humus over about 9 cm of humic sand (Stevens, 1968). Fish were not present at either clearwater site (M.R. Main, pers. comm.).

Plate 2.2. The two darkly-stained brownwater sampling sites in South Westland. Upper photo, Suspect Stream; lower photo, Steep Creek.

Table 2.2. Locations and some physical characteristics of sampling reaches (15-30 m long) in the five South Westland streams. Channel width and slope are expressed as means of five measurements with ranges in parentheses. Stability was assessed using the streambed component of the Pfankuch (1975) method which gives lower scores to more stable sites.

	Suspect Stream	Steep Creek	Mapourika Creek	Toilet Stream	Hidden Creek
Map reference (NZMS1 S71)	864902	870896	866831	821677	823671
Elevation (m asl)	95	80	110	230	250
Width (m)	2.4 (2.0-2.9)	2.3 (1.5-3.3)	4.6 (4.0-5.5)	1.4 (1.0-1.8)	1.4 (1.3-1.6)
Slope (°)	1 (0-2)	2 (1-3)	8 (3-16)	2 (1-4)	4 (1-5)
Approx. distance from source (m)	30	500	800	25	30
Pfankuch streambed stability score	39	42	35	42	22

Plate 2.3. The two clearwater sampling sites in South Westland. Upper photo, Hidden Creek (Franz Josef glacier in background); lower photo, Toilet Stream.

CHAPTER 3

SOURCES AND FLUXES OF DISSOLVED ORGANIC CARBON IN DEVELOPED AND UNDEVELOPED CATCHMENTS IN NORTH WESTLAND

3.1. INTRODUCTION

Although several workers have calculated organic carbon budgets for clearwater streams or rivers draining upland catchments (e.g., Fisher & Likens, 1973; McDowell & Fisher, 1976; Fisher, 1977), few have estimated fluxes in wetland areas where organic carbon export in drainage waters is substantially higher (Mulholland & Kuenzler, 1979). Estimates of annual DOC export in clearwater streams draining upland catchments rarely exceed 3 $g.m^{-2}$ (see Tate & Meyer, 1983), whereas export in streams flowing from wetland catchments is often greater than 5 $g.m^{-2}.y^{-1}$ (e.g., Grieve, 1984; McKnight *et al.*, 1985; Clair & Freedman, 1986). To my knowledge, only Mulholland (1981) has quantified inputs and outputs (total organic carbon) to a Northern Hemisphere wetland system, and nobody has documented the effects of wetland afforestation on DOC dynamics. Studies into the effects of development on DOC fluxes in upland catchments have been contradictory. For example, Hobbie & Likens (1973) found that DOC export was similar from streams in clear-cut and undisturbed Hubbard Brook catchments in New Hampshire, whereas Meyer & Tate (1983) demonstrated lower export from a clear-cut catchment at Coweeta, North Carolina.

About half of recent pine forest plantings in Westland, New Zealand, have been on pakihi wetlands most of which were v-bladed (see Section 2.1.6.) before planting to improve drainage (N.Z. Forest Service, 1984). Destruction of vegetation and alteration of natural drainage characteristics might be expected to have marked effects on the DOC dynamics of such catchments by removing potential sources of DOC and altering hydrological pathways. In this chapter, DOC budgets for three catchments of the Larry River Experimental Area (LREA), north of Reefton (see Section 2.2.2.) are presented. One catchment (L2) was undeveloped pakihi (predominantly manuka forest), whereas L1 and L3 were v-bladed and planted with pines in 1982 and 1985, respectively. My aims were to investigate major sources of DOC, to quantify DOC inputs and outputs from the three catchments, and to determine the effects of v-blading on DOC dynamics.

3.2. METHODS

3.2.1. DOC Analyses

All water samples were analysed for DOC within one week of collection by the micro-dichromate oxidation procedure (Maciolek, 1962; Newell, 1982) using heat-by-dilution. Each sample was analysed once, but triplicate analyses were carried out on one sample from each monthly batch to determine repeatability of the technique. Coefficients of variation (CV) for triplicate analyses ranged from 1.4 to 7.5 % and averaged 2.9 %.

Water was passed through 0.45 μm Millipore filters which had been leached for at least 24 hours in distilled water to remove soluble organics. Depending on suspected DOC concentration, 10-100 m*l* subsamples of water were evaporated (50-80^{o}C) to dryness in 250 m*l* flasks, after which remaining organics were oxidised with 5, 10 or 15 m*l* of 0.05 N potassium dichromate and concentrated sulphuric acid (2:1 acid:dichromate). After cooling, the solution was diluted with 100 m*l* distilled water followed by addition of phosphoric acid (1:1 dichromate:acid) to improve endpoint resolution during titration. Excess oxidant was titrated to a clear/green endpoint with 0.03 N ferrous sulphate after adding a few drops of barium diphenylamine sulfonate indicator. Reagent blanks were run routinely.

DOC concentration was calculated according to the method of Maciolek (1962):

(1) $$\text{DOC (mg)} = \frac{(A-B) \times N \times 8}{2.86}$$

where A = m*l* of ferrous sulphate used in blank titration;

B = m*l* of ferrous sulphate used in sample titration;

N = normality of ferrous sulphate;

8 = equivalent weight of oxygen;

2.86 = factor converting weight of oxygen to organic carbon.

Normality of ferrous sulphate (N) was calculated by titration against the potassium dichromate solution:

(2) $$N = \frac{\text{m}l \text{ dichromate} \times \text{normality of dichromate}}{\text{m}l \text{ ferrous sulphate used in titration}}$$

Maciolek (1962) recommended immersing the acid/dichromate mixture in a boiling water bath for three hours to facilitate maximum oxidation of organic carbon, and McCammon (1978) recovered an average of 98 % of organic carbon in beech (*Nothofagus*) detritus using this method. The heating step was omitted in the present study to enable rapid analysis of a large number of samples. To determine the oxidation efficiency of the modified technique, comparisons were made between the amounts of organic carbon extracted from beech detritus and tannic acid (Mallinkcrodt analytical reagent) by dichromate oxidation and ashing overnight at 500°C. Organic matter was assumed to be 50 % carbon (Maciolek, 1962).

The heat-by-dilution dichromate oxidation procedure retrieved an average of 83 % of organic carbon in tannic acid and beech detritus (Table 3.1.). DOC concentrations calculated from Equation 1 therefore were multiplied by 1.2 to provide a more accurate estimate of DOC. Lee *et al.* (1983) found that equivalent corrections were required when using heat-by-dilution dichromate oxidation to measure organic carbon content of some South Pacific soils. Thus, the equation used to calculate DOC can be simplified to:

(3) DOC (mg) = (A-B) x N x 3.36

Table 3.1. The percentage of organic carbon recovered from tannic acid and beech detritus using heat-by-dilution dichromate oxidation. The right hand column gives factors by which organic carbon values obtained by the Maciolek (1962) calculation must be multiplied to correct for inefficiency of oxidation. AFDW = initial ash-free dry weight of the compound oxidised.

Compound	AFDW (mg)	% recovery	Multiplication factor
Tannic acid	17.6	80.6	1.24
	20.0	85.1	1.18
	19.0	84.2	1.19
Beech detritus	28.7	86.2	1.16
	28.7	82.6	1.21
	28.7	79.1	1.26
Mean		83	1.2

3.2.2. Sample Collection

Sampling protocol and validation

Porous cup lysimeters and rainfall, throughfall and stemflow collectors were installed in the three experimental catchments on the Larry River pakihi (see Figs. 2.2. and 3.1.) in June-July 1986. Water samples from these and grab samples from streams were collected for DOC analyses at monthly intervals between 1 August 1986 and 31 July 1987, when volumes of rainfall and throughfall were also measured. Intensive storm sampling of streams was carried out for one week every month during summer (September 1986 to January 1987), and stemflow and soil water were sampled intensively between 16 and 23 December. Rainfall and stream discharge were recorded continuously by Forest Research Institute (FRI).

To determine if storing water samples in the field affected DOC concentrations, stemflow and soil water (lysimeter) samples from L2 were analysed before and after three weeks storage. Soil water samples from two horizons were kept *in situ* in lysimeters under zero vacuum and, after three weeks, no significant (t-test, $P > 0.05$; log (x) transformed) changes in DOC concentration were detected (Table 3.2.). Stemflow samples were stored in black, polyurethane bottles in the shade, and in opaque, polyethylene bottles in shaded and unshaded conditions to determine if photo-oxidation of DOC was occurring. No significant changes in DOC concentration between initial and stored samples were detected for any treatments after three weeks in the field (Table 3.2.).

Rainfall, throughfall and stemflow

Rainfall and throughfall were collected by plastic funnels (16 cm diameter) which drained into 20 *l* (rainfall) and 5 *l* (throughfall) polyethylene containers. The rainfall collector was located in a clearing in catchment L2, adjacent to a Lambrecht rain gauge operated by FRI (Fig. 3.1.). Five throughfall collectors were placed under manuka at L2, whereas at L1 throughfall was collected from beneath pines (2 collectors) and scrub (3) which was mostly bracken. Stemflow was collected from trunks of five pine (L1) and five manuka (L2) trees using plastic collars which channelled stemflow (10-20 cm above the ground) into storage containers.

To prevent contamination of samples by organic debris, all funnels and ends of stemflow collars were plugged with glass wool which was renewed monthly. Little organic debris was trapped by glass wool plugs in any collector at L1, but at L2, accumulations of manuka bark or leaves were

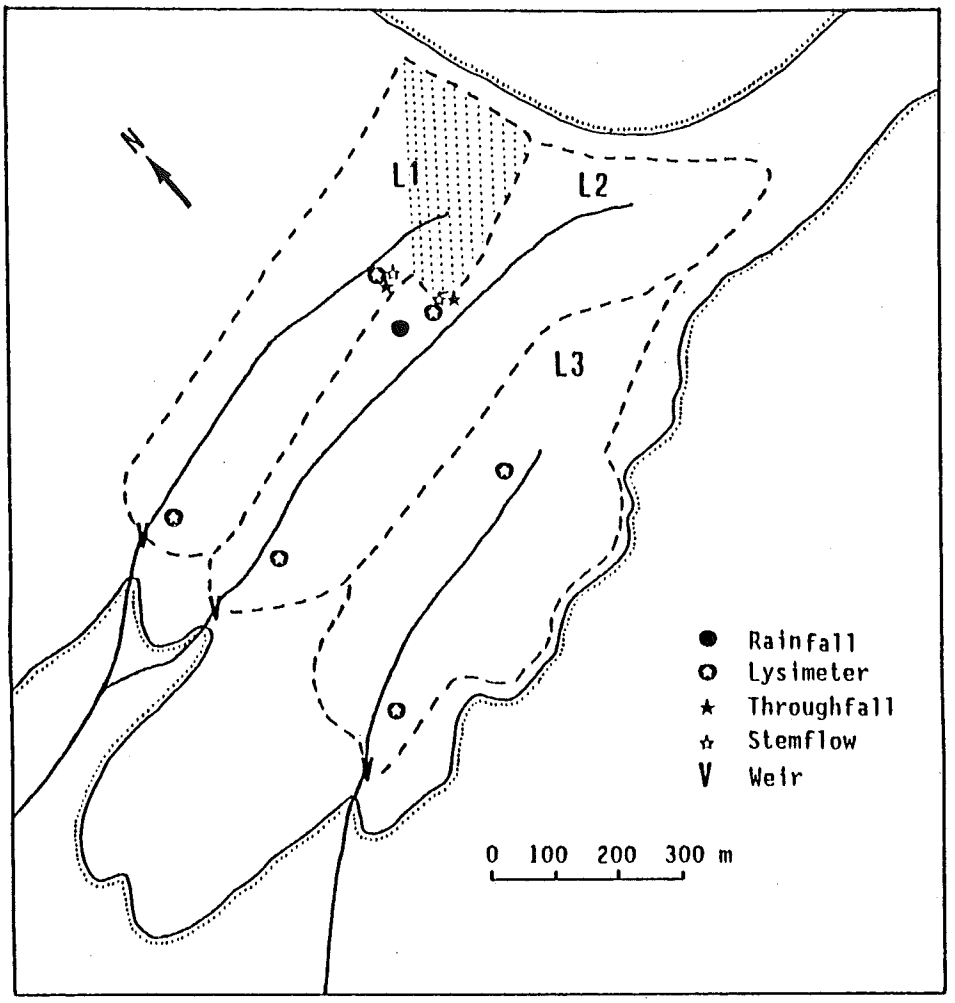


Figure 3.1. Locations of rainfall, throughfall, stemflow and soil water (lysimeter) collectors at catchments L1, L2 and L3 of the Larry River Experimental Area. Stream water samples were collected above v-notch weirs. Stippled area represents the 3.2 ha of manuka forest at L1.

Table 3.2. Concentrations ($\bar{x} \pm 2$ SE) of dissolved organic carbon (DOC) in stemflow (opaque or darkened bottles; shaded or unshaded conditions) and soil water samples from L2 before and after storage for three weeks in the field. All differences before and after storage were non-significant (t-test, $P > 0.05$; log (x) transformed).

Sample	DOC concentration ($g.m^{-3}$)	
	Before	After
Stemflow		
opaque, shaded	14.3 ± 1.2	13.1 ± 0.4
opaque, unshaded	14.3 ± 1.2	12.6 ± 0.7
darkened, unshaded	14.3 ± 1.2	13.1 ± 0.3
Soil water		
A horizon lysimeter	26.5 ± 0.5	25.5 ± 0.4
G horizon lysimeter	21.3 ± 0.7	22.0 ± 1.3

often found, particularly in throughfall funnels. Deionised water was run through three funnels and stemflow collars at L2 to determine how much DOC could be leached from "worst case" accumulations (four weeks) of organic matter. Deionised water gained on average 2.8 $g.m^{-3}$ DOC from throughfall funnels, but only 0.7 $g.m^{-3}$ from stemflow collars; DOC concentrations were not adjusted for contamination from organic material trapped in collectors.

Soil water

Sets of porous cup lysimeters (4 cm diameter) were installed in the upper and lower ends of catchments L1, L2 and L3 (Fig. 3.1.). Each set consisted of one lysimeter in A (~15 cm deep) and G (~33 cm) horizons of undisturbed Okarito soils (all catchments) and in v-blade mounds (~35 cm) at L1 and L3. Soil cores were taken before installation to ensure that lysimeter cups would be sampling the correct horizon, and lysimeter necks were jacketed with PVC tubing to prevent rainwater trickling down the sides. Lysimeters were evacuated (10-15 inches Hg) with a vacuum pump, sealed, and emptied under vacuum on the next sampling occasion.

Stream water

Grab samples of stream water were collected in polyethylene bottles (75 or 250 m*l*) above v-notch weir ponds in all catchments (Fig. 3.1.). Water stage height in meters (SH) was recorded at weirs concurrently and converted to discharge ($m^3.s^{-1}$) by the appropriate equation used by FRI hydrologists:

(4) Discharge = $1.38 \times SH^{2.5}$

In addition to monthly samples, 222 grab samples were taken from streams during storm events between September 1986 and January 1987; sampling frequency depended on discharge and its rate of change. Automatic samplers (Manning S200) operated by FRI also collected some water samples during storms, and 86 of them (taken between January and May 1987) were analysed for DOC.

3.2.3. Calculation of DOC Fluxes

Volumes of water entering each catchment annually as rainfall, throughfall, stemflow and soil water were calculated and multiplied by their mean DOC concentration (all sampling dates combined) to give annual DOC inputs per square meter of catchment. L2 and L3 are believed to be water tight, but catchment L1 probably loses some water through leakage from the stream channel where impervious subsoil pans may have been disrupted during v-blading (R.J. Jackson, FRI, Christchurch; pers. comm.). Thus, the difference between gross annual rainfall (i.e., measured above the vegetation canopy) and total runoff at L2 and L3 was attributed entirely to losses from interception (water evaporated from wet vegetation during or after rainfall), transpiration (water evaporated from dry leaves via stomata after being taken up from the soil and transported through stems), and evaporation from the soil.

Catchment L2

In L2 where the forest vegetation is evergreen, the percentage of rainfall intercepted was assumed to be constant in all months (27 %) and was calculated from the mean difference between rainfall and runoff in June and July (1986 and 1987) when transpiration was assumed to have been negligible. The difference between net rainfall (i.e., gross rainfall minus interception) and runoff represents the amount of water lost annually by transpiration (44.7 m^3x10^3; Table 3.3.).

The proportion of rain entering L2 as throughfall (33 %) was estimated from volumes in collectors, and the difference between throughfall and net rainfall was attributed to stemflow from manuka (40 %). These proportions are similar to those of Blake (1965) who estimated interception losses of 31 %, and throughfall and stemflow fluxes of 38 % and 31 % of rainfall, respectively, in a stand of manuka in Northland. Aldridge & Jackson (1968) calculated interception and throughfall by manuka in the southern North Island as 39 % of rainfall, whereas stemflow was 23 %.

Catchment L1

Inputs and losses of rainfall from L1 were calculated separately for the 3.2 ha of manuka forest (as described for L2), and the 6.8 ha of v-bladed catchment. Bare v-blade tracks cover about one third of the developed area at L1 whereas the remaining two thirds (v-blade mounds and undisturbed soil between mounds) are vegetated. Rainfall was partitioned

into volumes falling on and between mounds (99.5 m^3x10^3) and on to tracks (49.0 m^3x10^3). Some of the latter (~18.4 m^3x10^3) is likely to be evaporated from the tracks, whereas the remainder runs quickly into the stream channel (R.J. Jackson, pers. comm.), and would have little opportunity to leach DOC from soil or vegetation.

Mapping of six, 20 m transects at L1 showed that pine foliage formed a partial canopy over 22 % of v-blade mounds and undisturbed soil between mounds at L1. Scrub (mostly bracken) covered the entire area on and between mounds, and grew right to the base of pine trees, further enriching pine throughfall with DOC. Interception by pine and scrub (15 %) was calculated from the difference between gross rainfall and volumes of throughfall (measured in collectors) plus stemflow from pines (taken as 6 % of gross rainfall). The latter value is in the middle of the range (4-9%) given by Whitehead & Kelliher (1986) for stemflow from pines (11-12 years old) in two plantations (334 and 754 stems ha^{-1}) near Rotorua, North Island. Whitehead & Kelliher (1986) calculated interception as 15-18 % (c.f., 15 % in the present study) and throughfall as 73-81 % of rainfall for the same two plantations. Their throughfall values are slightly lower than the 84 % of gross rainfall collected in throughfall collectors under pine and scrub at L1. Annual fluxes of DOC in pine stemflow and throughfall were adjusted for the proportion of developed, vegetated catchment area covered by pines (22 %).

Annual transpiration losses of water from the developed area of L1 were taken as 29.2 m^3x10^3 (R.J. Jackson, pers. comm.), and the difference between these and all other water losses during the study period was assumed to be due to leakage from the stream channel (12.8 m^3x10^3). Runoff volumes were assumed to be the same from v-blade mounds and soils between mounds.

Catchment L3

Losses of rainfall from L3 by interception and transpiration would have been negligible during the study period because vegetation cover was sparse for most of the time. Indeed, losses at L3 were almost identical for the year immediately following development (January 1985 to December 1986) when vegetation had been cleared from the catchment (42 % of rainfall lost), and for the twelve months of the present study (46 %). Thus for budgetary purposes, the difference between annual rainfall and runoff at L3 was attributed to evaporation from the soil. Because of the sparse vegetation cover at L3, soil surfaces were often exposed to the evaporative

effects of direct sunlight and wind. Runoff from L3 was assumed to have been derived in equal proportions from v-blade tracks, mounds and undisturbed soils (i.e., one third from each).

Outputs

Annual outputs of DOC from streams were estimated from flow duration data (provided by FRI) and DOC:discharge relationships for each catchment. Flow durations were divided into 54-59 classes (number depending on flow magnitude) ranging in size from 0.02 $l.s^{-1}.ha^{-1}$ for low flow classes (< 0.1 $l.s^{-1}.ha^{-1}$) to increments of 2.5 $l.s^{-1}.ha^{-1}$ for flow size classes exceeding 20 $l.s^{-1}.ha^{-1}$. Mean DOC concentrations for each flow size class were calculated from DOC:discharge regression equations (see Section 3.3.1.), and were multiplied by the proportion of time spent in that size class during the study period. Where r^2 values for regressions were very low (i.e., for low discharge data sets at L1 and L2; see Equations 7 & 8 in Section 3.3.1.), means of all low flow size classes were averaged to calculate DOC concentration. Discharge weighted DOC values for each size class were summed to give mean annual DOC concentrations for each stream, and these values were multiplied by the volume of runoff to give amounts of DOC (g) exported per square meter of catchment per year.

Table 3.3. Water budgets (m^3x10^3) calculated for L2 (control), L1 (5 yr post v-blading) and L3 (2 yr post v-blading) between August 1986 and July 1987. Gross rainfall during this period was 218.5 cm. Where appropriate, fluxes of water through soils were calculated for undisturbed A and G horizons (both combined), v-blade mounds and v-blade tracks. Negative values represent a net loss of water. -, not applicable.

	L2	L1	L3
Interception			
manuka	-68.4	-18.9	-
pine/scrub	-	-14.9	-
Throughfall			
manuka	83.6	23.1	-
pine	-	18.4	-
scrub	-	83.6*	-
Stemflow			
manuka	101.4	28.0	-
pine	-	1.3	-
Transpiration			
manuka	-44.7	-12.3	-
pine/scrub	-	-29.2	-
Leakage	-	-12.8	-
Soil water			
A + G	140.4	21.4 + 38.7**	39.7
mounds	-	21.4	39.7
tracks	-	30.6	39.7
Evaporation	-	-18.4	-99.5
Runoff	140.4	112.0	119.0

*, includes water falling through pine foliage and then scrub.

**, volumes of water assumed to pass through undisturbed soils beneath scrub (21.4 m^3x10^3) and manuka forest soils (38.7 m^3x10^3).

3.3. RESULTS

3.3.1. DOC Concentrations

Rainfall and throughfall

DOC concentration in rainwater measured at monthly intervals ranged from 0.5 to 1.8 $g.m^{-3}$ and averaged 1.0 $g.m^{-3}$. At L1 (v-bladed and planted with pines in 1982), passage of rain through pine foliage elevated mean DOC concentrations to between 2.6 and 16.1 $g.m^{-3}$ (Fig. 3.2.), and even higher levels were recorded in throughfall under scrub (6.1-31.8 $g.m^{-3}$). The highest DOC concentrations in throughfall (up to 55.3 $g.m^{-3}$) were obtained under manuka at the control catchment (L2).

The concentration of DOC in throughfall peaked in December under all types of vegetation, although high values (> 30 $g.m^{-3}$) were also recorded under scrub at L1 in samples collected on 1 August 1986 (Fig. 3.2.). In the five months prior to January, DOC concentration varied considerably in all sets of collectors except under pine. For example, the range of concentrations observed under manuka was 6-55 $g.m^{-3}$. However, in the latter half of the study (January to July 1987) mean concentrations were much more similar in any set of collectors, the range under manuka, for example, being 8-23 $g.m^{-3}$. Monthly DOC concentrations in throughfall from manuka at L2 and scrub at L1 were inversely correlated with rainfall volumes during the same periods (r_s = -0.60 and -0.69, respectively; $P < 0.05$), indicating that amount of rainfall was an important factor influencing DOC concentration in throughfall.

Stemflow

DOC concentration in stemflow from pines (L1) peaked in November-December at about 20 $g.m^{-3}$, but on most other dates values were less than 10.0 $g.m^{-3}$ (Fig. 3.3.). Manuka stemflow always had mean DOC concentrations greater than 15 $g.m^{-3}$ but did not show the same temporal pattern as pine stemflow. Although a small peak in manuka stemflow DOC concentration was found in December, values found in early and late July were 2-3 times greater and had a peak of 152.8 $g.m^{-3}$.

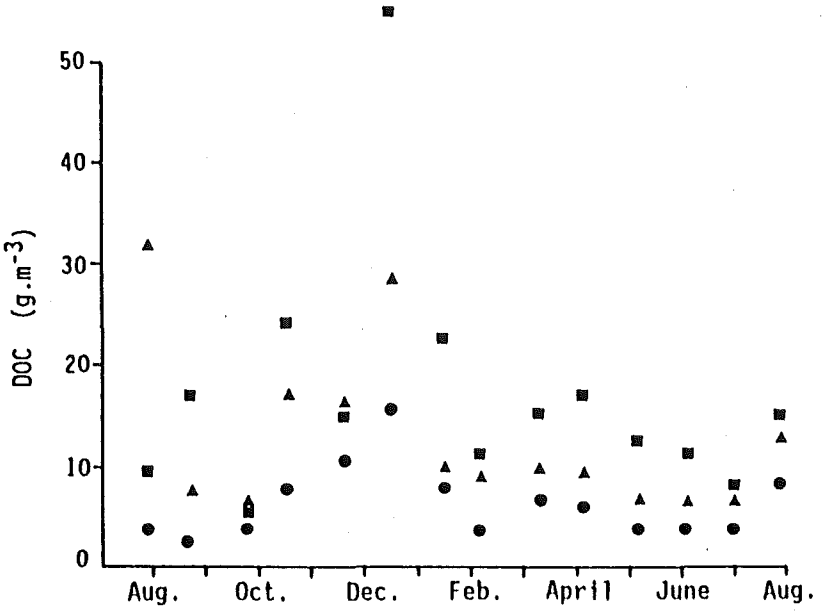


Figure 3.2. Mean monthly concentrations of DOC in throughfall under pine (●) and scrub (▲) at L1, and manuka (■) at L2 between August 1986 and July 1987. Coefficients of variation for replicate samples averaged 35, 38 and 19 % for manuka, scrub and pine, respectively.

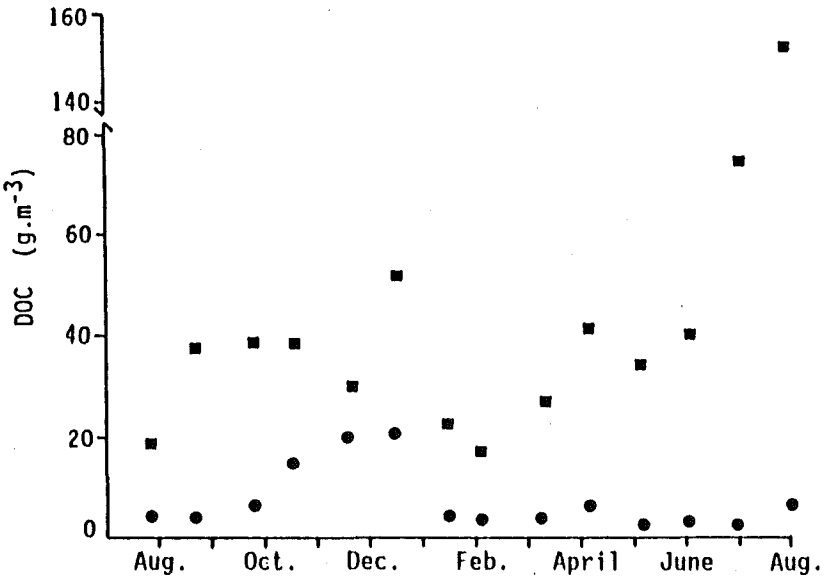


Figure 3.3. Mean monthly concentrations of DOC in pine stemflow at L1 (●) and manuka stemflow at L2 (■) between August 1986 and July 1987. Coefficients of variation for replicate samples averaged 40 % for pine and 23 % for manuka

Samples of stemflow from one pine tree (L1) and one manuka (L2) were collected after a series of rainfall events between 16 and 23 December when a total of 4.2 cm of rain was recorded (Fig. 3.4.). During this time, DOC concentrations in pine stemflow varied from 9.0 to 27.3 $g.m^{-3}$ and were lowest during the heaviest period of rainfall. Manuka stemflow DOC was also lowest (27.1 $g.m^{-3}$) during the same storm event and was highest (76.1 $g.m^{-3}$) following an extended period (~14 hours) of relatively light rainfall on 18-19 December (Fig. 3.4.). Thus, even though summer peaks in stemflow DOC were detected by routine monthly sampling, it is important to realise that concentrations were also affected by the frequency and intensity of rainfall.

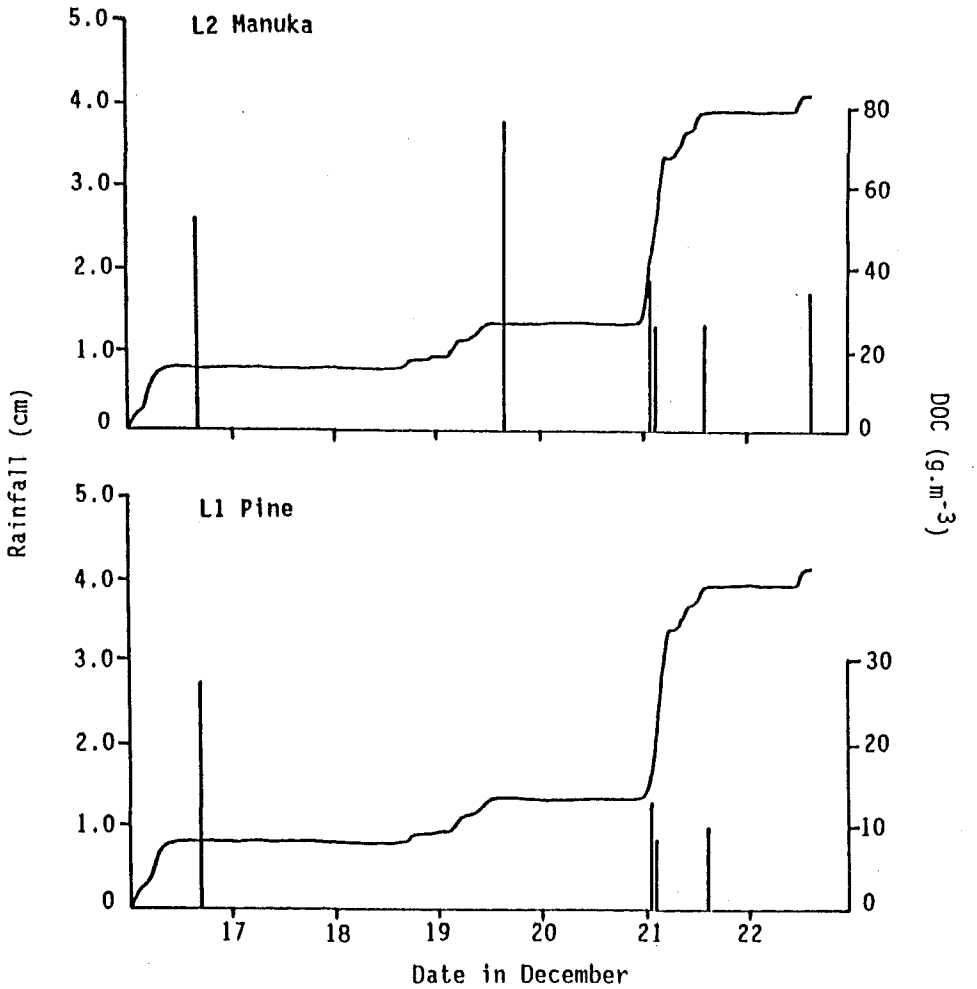


Figure 3.4. Changes in concentrations of stemflow DOC for manuka at L2 and pine at L1 during a series of rainfall events between 16 and 23 December 1986. Continuous line = cumulative rainfall; vertical lines = DOC concentration.

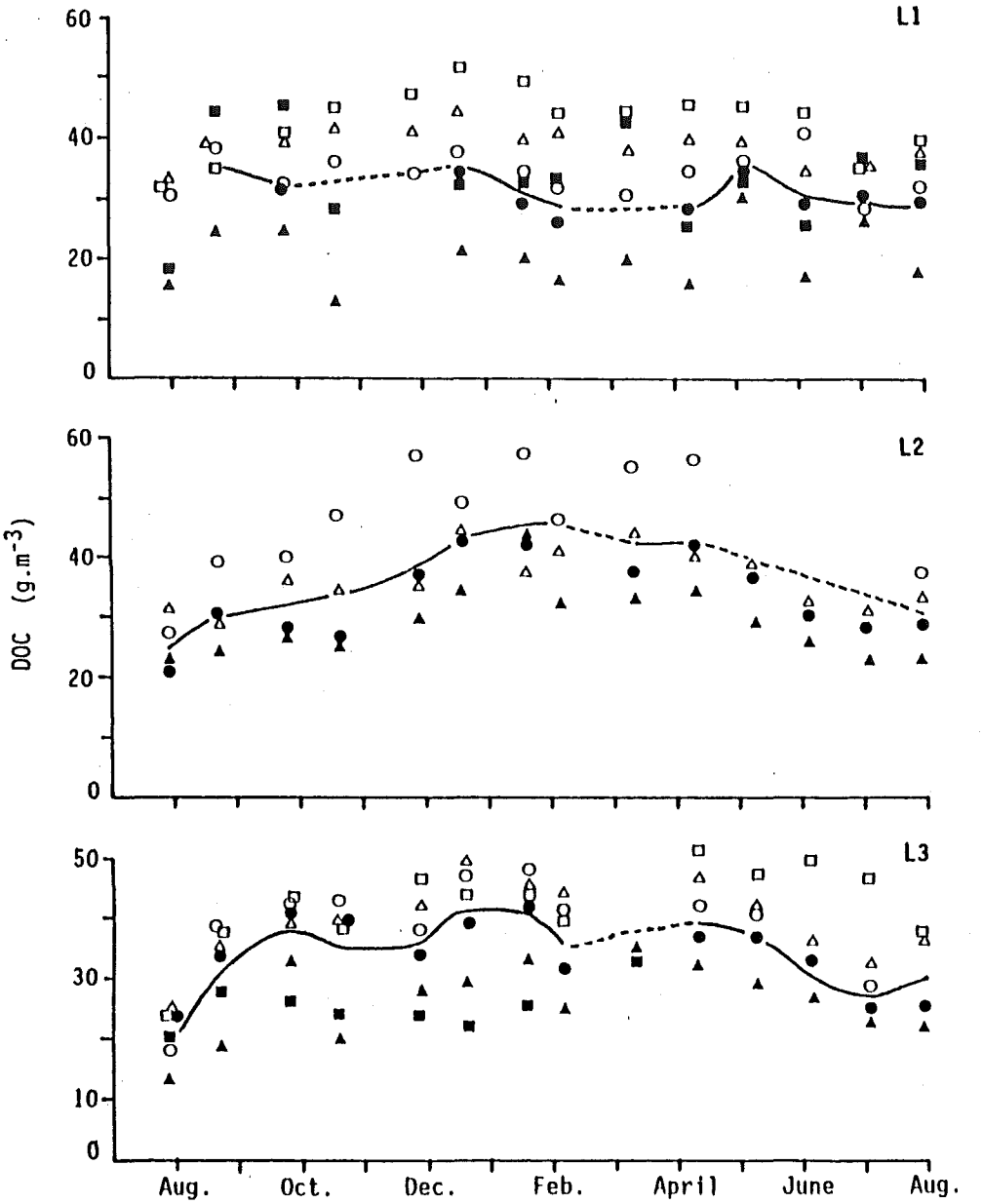


Figure 3.5. Monthly concentrations of DOC in soil water at the three Larry River catchments obtained from lysimeters in A horizons (circles), G horizons (triangles) or v-blade mounds (squares). Open and closed symbols represent upper and lower catchment lysimeters, respectively. Lines connect means for undisturbed soils (A + G horizons, upper + lower catchment) on each date and are broken between dates when some lysimeter samples were missing.

Soil water

DOC concentrations in lysimeter samples varied between soil types (A horizon, G horizon, mounded earth) and catchment locations (upper or lower) on most dates (Fig. 3.5.). In general, concentrations were less in lower catchment samples than in samples from the upper parts of catchments. At L2 (control), concentrations in A horizons (21.2-57.0 $g.m^{-3}$) were almost always greater than in G horizons (22.9-44.0 $g.m^{-3}$) for any pair of lysimeters, but at other sites this trend was consistent only for lower catchment samples (Fig. 3.5.). At L1 and L3, DOC minima of about 13 $g.m^{-3}$ were recorded in G horizons (October and August 1986, respectively), and maxima of 51 $g.m^{-3}$ were found in mounded earth (December (L1) and April (L3)). Seasonal changes in DOC concentration were not as apparent in the developed catchments (L1 and L3) as at L2 where concentrations in most lysimeter samples were higher (minima > 30 $g.m^{-3}$) between December and April than in other months (minima 20-30 $g.m^{-3}$) (Fig. 3.5.).

Water samples were collected from lower catchment lysimeters at L2 and L3 at 9 to 25 hour intervals between 16 and 23 December when a total of 4.2 cm of rain fell (Fig. 3.6.). During this time, DOC concentrations in samples from any one lysimeter were relatively constant (range of CVs = 6.3-18.4 %), indicating that soil water DOC was not affected greatly by the intensity or duration of rainfall.

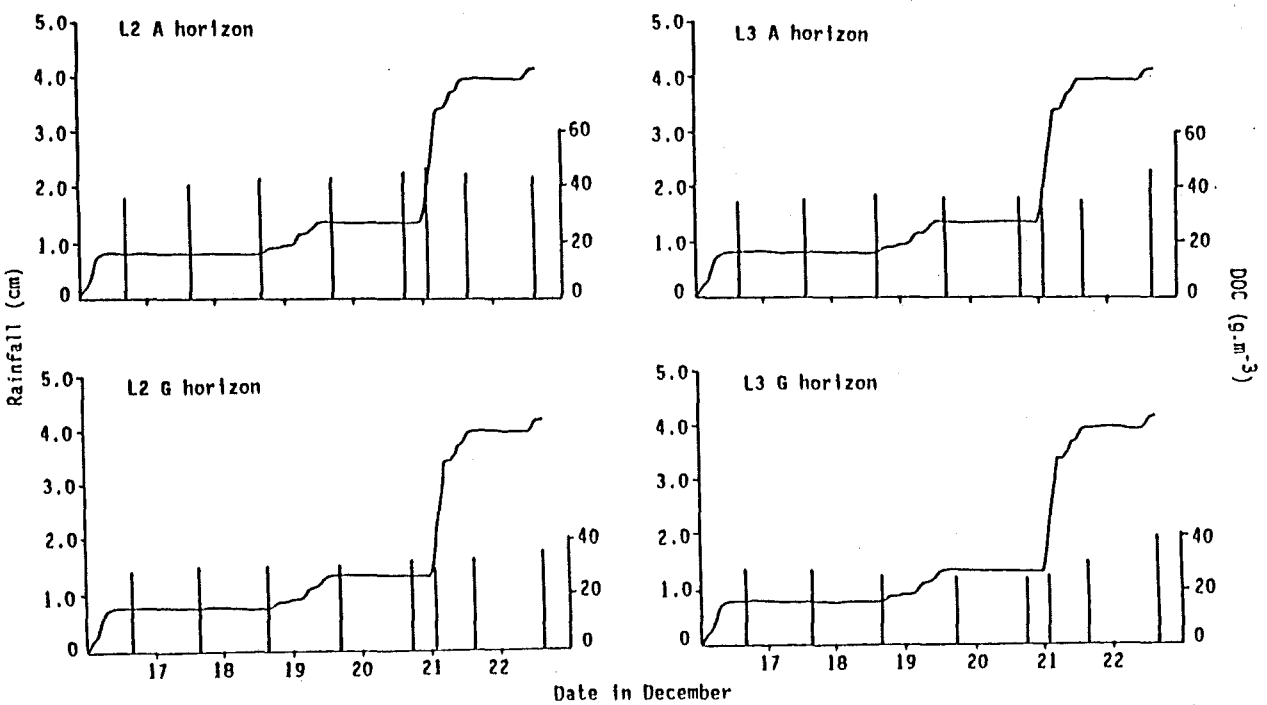


Figure 3.6. Concentrations of DOC in soil water from A and G horizons at L2 and L3 at 9-25 hour intervals between 16 and 23 December 1986. Continuous line = cumulative rainfall; vertical lines = DOC concentration.

Stream water

DOC concentrations in monthly grab samples ranged from 7.0 to 41.2 $g.m^{-3}$ in the stream draining the more recently developed catchment (L3), but were less variable in L1 and L2 (17.9-38.0 $g.m^{-3}$) (Fig. 3.7.). Seasonal patterns in DOC concentration were not apparent in any stream. Lowest concentrations were recorded during intensive summer storm sampling (12.4, 16.8 and 4.3 $g.m^{-3}$ in L1, L2 and L3, respectively) when stream water clearly included a substantial volume of immediate surface runoff.

Two DOC:discharge patterns were detected at all sites. DOC concentration generally increased with increasing discharge up to about 1.0 $l.s^{-1}$, although r^2 values for these relationships were low at L1 and L2. Regression equations describing the relationships between DOC ($g.m^{-3}$) and log (x+1) discharge (D) for low flow data sets (< 1.0 $l.s^{-1}$) are:

(7) L1 DOC = 3.5D + 30.0 r^2 = 0.02

(8) L2 DOC = 22.9D + 28.4 r^2 = 0.12

(9) L3 DOC = 116.0D + 11.6 r^2 = 0.58

At flows ≥ 1.0 $l.s^{-1}$, negative relationships between DOC concentration and discharge were found at all sites, and are described by the equations:

(10) L1 DOC = -6.8D + 34.1 r^2 = 0.45

(11) L2 DOC = -6.1D + 36.9 r^2 = 0.37

(12) L3 DOC = -11.2D + 41.9 r^2 = 0.63

DOC concentration in stream water at equivalent discharges above 1.0 $l.s^{-1}$ was 3-4 $g.m^{-3}$ higher in L2 than L1. However, streamwater DOC concentration in L3 was greater than in the control stream (L2) at discharges between 1.0 and about 8.0 $l.s^{-1}$, but slightly lower at flows greater than this.

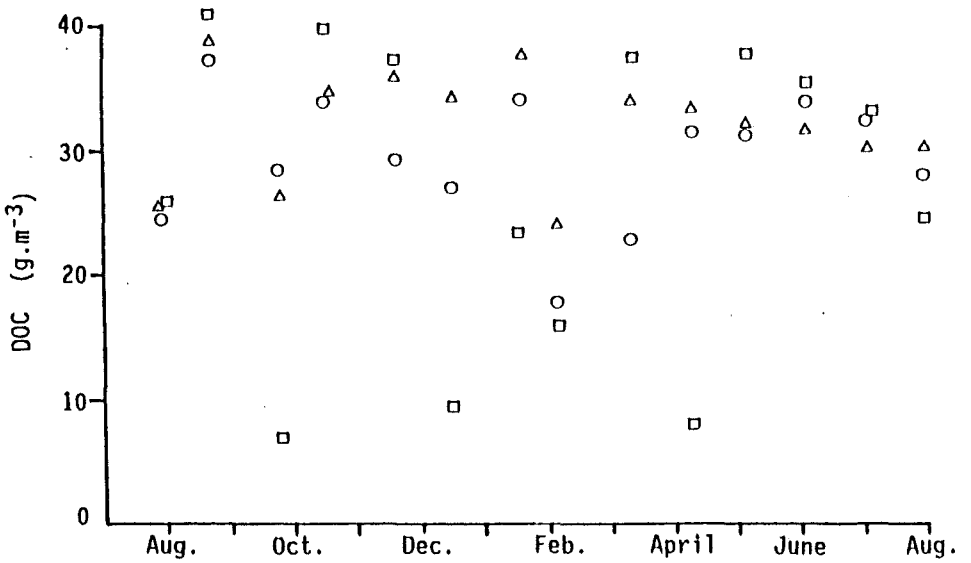


Figure 3.7. Concentrations of DOC in monthly grab samples taken from streams draining catchments L1 (○), L2 (△) and L3 (□) between August 1986 and July 1987.

3.3.2. DOC Fluxes

Total soil water inputs of DOC were highest to the control catchment (L2) and lowest to the developed catchments (v-bladed and planted with pines in 1982 and 1985) (Table 3.4.). Manuka stemflow was a major source of DOC at L2 where it contributed 76 % of the DOC inputs from vegetation (i.e., throughfall + stemflow). At L1, only 41 % of DOC inputs from vegetation came from the v-bladed section even though it represents 68 % of total catchment area. Of the vegetation inputs, stemflow and throughfall from pines contributed less than 5 %; most inputs from the developed area came from scrub throughfall on and between v-blade mounds (Table 3.4.).

Where land had been v-bladed, water running off tracks made little contribution to overall DOC inputs to streams; most came from v-blade mounds and undisturbed soils between mounds (Table 3.4.). Because of the sparse vegetation cover at L3, virtually all the DOC in stream water there could be attributed to leaching from soil organic matter on and between v-blade mounds.

DOC inputs in soil water at L3 were almost identical to amounts exported in stream water. In contrast, DOC export at L1 exceeded calculated inputs to the stream by about 4.44 $g.m^{-2}.y^{-1}$ and the excess may be attributable to leachates produced by the extensive moss community in the stream itself. However, this was not apparent in L2 where calculated inputs exceeded export by 5.33 $g.m^{-2}.y^{-1}$ (but see Discussion). Annual export of DOC in stream water (28.68-37.75 $g.m^{-2}$) was highest from the control catchment (L2), and lowest from L3 (Table 3.4.).

Table 3.4. Mean annual concentrations and fluxes of DOC inputs via rainfall, throughfall, stemflow and soil water, and outputs in stream water for catchments L2 (control), L1 (5 yr post v-blading) and L3 (2 yr post v-blading) between August 1986 and July 1987. Where appropriate, soil water DOC concentrations were calculated for undisturbed A and G horizons (both combined), v-blade mounds and v-blade tracks. Mean DOC concentrations in stream water were calculated from flow duration data and DOC:discharge regressions. Numbers in parentheses are 2 SE. -, not applicable.

	L2		L1		L3	
	Conc, $g.m^{-3}$	Flux $g.m^{-2}.y^{-1}$	Conc, $g.m^{-3}$	Flux $g.m^{-2}.y^{-1}$	Conc, $g.m^{-3}$	Flux $g.m^{-2}.y^{-1}$
Rainfall and vegetation inputs:						
Rain	1.0 (0.2)	2.19	1.0 (0.2)	2.19	1.0 (0.2)	2.19
Throughfall						
manuka	17.9 (3.6)	12.91	17.9 (3.6)	4.13	-	-
pine	-	-	6.5 (1.4)	1.20	-	-
scrub	-	-	12.7 (3.1)	10.62	-	-
Stemflow						
manuka	46.0 (9.3)	40.20	46.0 (9.3)	12.87	-	-
pine	-	-	7.9 (1.7)	0.10	-	-
Total vegetation inputs		53.11		28.91		-
Soil water inputs:						
A + G	35.6 (2.5)	43.08	31.3* (2.2)	20.48	34.2 (2.3)	13.58
mounds	-	-	38.1 (3.1)	8.15	36.8 (4.9)	14.61
tracks	-	-	1.0 (0.2)	0.31	1.0 (0.2)	0.40
Total soil water inputs		43.08		28.94		28.59
Outputs:						
Stream water	31.2	37.75	29.8	33.38	24.1	28.68

*, mean DOC concentration in water from undisturbed soil under scrub. DOC flux through undisturbed soils in L1 was adjusted for the proportion of rain falling through manuka forest (13.78 $g.m^{-2}.y^{-1}$) and scrub between v-blade mounds (6.70 $g.m^{-2}.y^{-1}$).

3.4. DISCUSSION

Sources of DOC

Between August 1986 and July 1987, inputs of DOC from vegetation were almost twice as high to the control (L2) as to catchment L1 (v-bladed and planted with pines in 1982). At L1, manuka forest covered only 3.2 of the 10 ha but accounted for about 59 % of total inputs from vegetation. An important contributor to the high DOC concentrations of manuka stem leachates may have been the large population of scale insects which infest trees and excrete honeydew that can contain up to 81 % sugar (Gaze & Clout, 1983). Season, rainfall intensity and rainfall duration were major factors influencing concentrations of DOC in stemflow and throughfall. This is probably because exudates such as honeydew are produced seasonally, and leachates are diluted by rainfall. Mulholland (1981) also reported seasonal variations in organic carbon concentrations in throughfall and stemflow from maple, ash and gum trees in Creeping Swamp, North Carolina, and attributed them to the growth cycle of the trees.

Despite low levels of DOC in stemflow and throughfall entering the developed area of L1 (i.e., via pine and scrub), mean DOC concentrations in soil water were only slightly lower than at the control catchment. Indeed, DOC concentrations in soils at L2 were remarkably similar to undisturbed soils at L3 where inputs via throughfall and stemflow were negligible because of sparse vegetation cover. Soils at LREA appeared to be able to generate considerable amounts of DOC from within, presumably through decomposition of soil organic matter by microbes. Mean DOC concentrations of water in v-blade mound soils at L1 and L3 were slightly higher than in undisturbed soils between mounds. V-blade mounds contain much woody material, including branches and stems buried after crushing and burning, and these are probably sources of additional DOC.

Implicit in my calculations of total soil water DOC inputs (see Table 3.4.) is the assumption that all rain water not lost through interception, transpiration or evaporation (and not falling on to v-blade tracks) passes through soils before entering the stream channel. Although this is likely to be correct at L1 and L3 where v-blade mounds are always unsaturated (Jackson, 1987) and where rain water falling on to undisturbed soils is effectively impounded between mounds, it may not always be the case in the control catchment. The water table at L2 rises quickly during rainfall (usually only 1.0-2.0 cm resaturates the soil) and large surface pools which

can cover up to 50 % of the land are formed (Jackson, 1987). Water moves slowly between pools through and under surface vegetation, and much presumably enters stream channels without passing through soil horizons. Thus, only a small proportion of the DOC flux attributed to soil water at L2 may in fact come from that source, and total soil water inputs to the catchment are likely to be over-estimated. This might partly explain the contrasting findings that DOC input exceeded export at L2 but not at L1.

DOC in stream water

Maximum DOC concentrations recorded in streams draining the three Larry River catchments (38-41 $g.m^{-3}$) were slightly lower than the maximum of 47 $g.m^{-3}$ cited by Gorham *et al.* (1984) for some North American peatland waters. In the present study, concentrations were least variable in the control stream and most variable in the stream draining the more recently developed catchment (L3). L2 and L3 streams also had the highest (31.2 $g.m^{-3}$) and lowest (24.1 $g.m^{-3}$) mean annual DOC concentrations, respectively, indicating that development had marked effects on their DOC dynamics.

DOC:discharge relationships showed the same pattern in all streams; DOC increased with discharge up to about 1.0 $l.s^{-1}$ and thereafter a negative relationship was found. Several workers have reported significant positive correlations between DOC and discharge (e.g., McDowell & Fisher, 1976; Meyer & Tate, 1983; Grieve, 1984), apparently because of increased leaching of organic matter from vegetation and soils by rainfall. Others have noted negative correlations (e.g., Fisher, 1977; Clair & Freedman, 1986), whereas Hobbie & Likens (1973) found no "obvious overall relationship" between DOC and discharge in two Hubbard Brook streams. To my knowledge, the only other worker to document positive and negative correlations at the same site is Mulholland (1981) who found that organic carbon (DOC + fine particulates) in Creeping Swamp increased during storms, but that seasonal variations overrode the effects of floods and resulted in an overall negative relationship.

The two relationships found at the LREA sites can be attributed to changing hydrological pathways. At peak flows, a large proportion of water entering the L2 stream comes from overland flow (discussed in previous section) and as a result it is likely to be lower in DOC than soil water. At L1 and L3 on the other hand, DOC concentrations in stream water during periods of high flow are low probably because a large proportion of the runoff comes from bare v-blade tracks where the potential to pick up DOC

is low. As discharge declines, the proportion of water entering streams from the soil increases and DOC concentration will rise again. However, as flows drop below 1.0 $l.s^{-1}$, some water may pass through B horizons where organic carbon can precipitate out (Ross *et al.*, 1977). This results in a lowering of stream water DOC concentration during very low flows. Differences in DOC:discharge relationships between L1 and L2 can be attributed to greater DOC inputs from vegetation and soil water at the latter site, and low-DOC water entering the stream at L1 from v-blade tracks. The higher slope and intercept of the high flow DOC:discharge equation for L3 may be a consequence of the greater contribution of soil water DOC at flows less than between 1 and about 8 $l.s^{-1}$, and higher inputs of low-DOC water from v-blade tracks at flows greater than that.

A major problem when estimating DOC export from relationships with discharge is that regression equations may account for only a small proportion of the variation in stream water DOC concentration. Discharge explained over half of the variation in DOC concentration in low and high flow data sets at L3, but r^2 values at L1 and L2 were much smaller, particularly for low flow data sets. Grieve (1984) found that inclusion of a seasonal variable markedly improved regressions (from $r^2 = 0.39$ to $r^2 = 0.82$) for a moorland stream in Scotland. However, no seasonal trends in stream water DOC were apparent in the present study, and the reasonably strong DOC:discharge relationship detected at L3 suggests that poor correlations were related more to differences within catchments. An important factor may have been that DOC concentrations were higher on the falling limb of the hydrograph than on the rising limb at equivalent discharges for a given storm event, sometimes by as much as 20 $g.m^{-3}$ (as indicated by two storms analysed in December and January). This is the reverse of hysteresis effects reported by Schlesinger & Melack (1981) who suggested that organic carbon concentrations are likely to be higher on the rising limb. The finding of a greater DOC concentration on the falling limb supports the hypothesis that more water is derived from soils as stream flows drop.

Export of DOC

A critical factor affecting calculation of mean annual DOC concentration in stream water was the proportion of time spent in the lowest flow size class. For almost half the study period, flows at L3 were less than 0.2 $l.s^{-1}$, and DOC concentration averaged 16.2 $g.m^{-3}$. Consequently, the L3 stream had the lowest annual DOC export (28.68 $g.m^{-2}$). In contrast, 37 % of the time was spent in the lowest flow size class at L1 but only 14 % of the time at L2 (FRI, pers. comm.) which had the highest DOC export (37.75 $g.m^{-2}.y^{-1}$). Because all flow size class means less than 1.0 $l.s^{-1}$ at L1 and L2 were averaged to estimate low flow DOC fluxes, mean annual DOC concentrations in these streams might have been overestimated slightly.

Annual DOC export in upland clearwater streams in North America rarely exceeds 3 $g.m^{-2}$ (see Tate & Meyer, 1983), but values in brownwater streams are much higher. For example, McKnight *et al.* (1985) estimated DOC export of 8.4 $g.m^{-2}.y^{-1}$ from Thoreau's Bog, Massachusetts (mean DOC = 35 $g.m^{-3}$), whereas Clair & Freedman (1986) calculated DOC export of 5.1-13.6 $g.m^{-2}.y^{-1}$ for four brownwater streams in Nova Scotia, Canada. Naiman (1982) suggested that upstream beaver activity may have contributed to the very high DOC export (48.38 $g.m^{-2}.y^{-1}$) recorded from Beaver Creek in Quebec. Mulholland & Kuenzler (1979) described a linear relationship between runoff and total organic carbon (on average about 93 % DOC) export in wetland waters of North Carolina that was considerably different from the relationship for clearwater streams draining upland catchments, and Meyer (1986) found that DOC export and runoff from two "blackwater" rivers in Georgia, southeastern United States, had a similar linear relationship. Adding data from several other studies (including the present one) to those of Meyer (1986) and Mulholland & Kuenzler (1979) yields the following equation that describes the relationship between runoff (cm) and DOC export ($g.m^{-2}.y^{-1}$) in brownwater streams (Fig. 3.8.):

(13) $\quad \text{Export} = 0.13\ \text{Runoff} + 1.23 \qquad r^2 = 0.66$

The slope and intercept of this equation are slightly higher than those given by Mulholland & Kuenzler (1979) (0.12 and 0.72, respectively), but suggests that the relationship between these parameters is universally predictable.

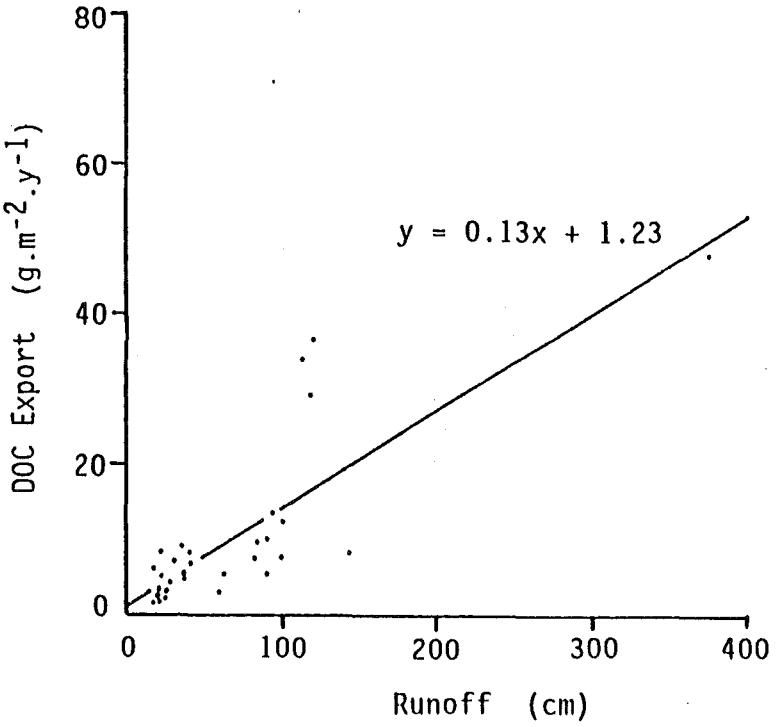


Figure 3.8. Relationship between DOC export and runoff from catchments (mostly wetland) giving rise to brownwater streams and rivers. Data come from the present study, Mulholland & Kuenzler (1979), Schlesinger & Melack (1981), Naiman (1982), Grieve (1984), McKnight *et al.* (1985), Clair & Freedman (1986), and Meyer (1986).

DOC mass balance

The difference between total DOC input and export represents the net balance between in-stream losses and production. Losses of DOC can occur through microbial uptake (Lock & Hynes, 1976; Kaplan & Bott, 1983), abiotic adsorption to surfaces (Dahm, 1981; Weber *et al.*, 1983), and through precipitation (Lush & Hynes, 1973; Petersen, 1986), whereas DOC can be produced by leaching, secretion and excretion of soluble compounds from algae, macrophytes and leaf litter which occur in the stream channel (e.g., McDowell & Fisher, 1976; Mulholland, 1981). In the present study, direct inputs of allochthonous litter would not have been important because the only stream with overhanging vegetation (L2) ran underground for much of its length (see Section 2.2.2.).

The only potential in-stream sources of DOC evident at L3 were algae on stones and rushes growing in the channel, but they were not abundant and therefore were unlikely to have contributed significantly to DOC flux. Thus, it is not surprising that no net difference between total DOC inputs and exports was recorded at L3. In contrast, vegetation (mostly moss) filled much of the stream channel at L1 where up to 13 % of DOC exported may have come from bryophytes and associated algae in the stream channel.

DOC fluxes calculated for the control catchment indicated that the stream was a net receiver of DOC, but it should be remembered that estimates of inputs to the L2 stream may have been subject to error because of the large amount of overland flow entering the stream channel during storm events (discussed earlier).

Effects of catchment development on DOC dynamics

Despite destruction of manuka forest, an important source of DOC, developed catchments appeared to generate considerable amounts of DOC within their soil profiles. This material was presumably derived from decomposing organic matter which would have been supplemented by branches and stems buried during v-blading. Overall, however, total DOC inputs to the L1 and L3 streams were much lower than to the control, and this is undoubtedly a reflection of vegetation removal and drainage works. Of particular importance appeared to be the mounding of soil during v-blading, a practice which effectively transformed one third of the catchment area from uncompacted soil (apparently the major source of DOC) to impermeable v-blade tracks where potential DOC sources were few. Meyer & Tate (1983) also reported reduced DOC inputs to a stream at Coweeta two years after clear-cutting, and attributed this to lower inputs from riparian vegetation, subsurface water, and in-stream DOC sources.

Amounts of DOC exported in stream water were highest from the control and lowest from the more recently developed catchment. Similarly, Meyer & Tate (1983) reported that DOC exported from a Coweeta catchment clear-cut two years previously was only 70 % of that exported from the reference watershed even though runoff was similar. On the other hand, Hobbie & Likens (1973) found that DOC export was similar in developed (clear-cut 3-4 years before the study) and undisturbed catchments in Oregon, despite a 26 % increase in runoff from the clear-cut site, and Dahm (1980; cited in Meyer & Tate, 1983) reported an increase in DOC export from a clear-cut catchment in Oregon. Comparisons between L1 and L3 suggest that the time elapsed since development was a significant factor influencing DOC dynamics, an observation that is consistent with Dahm's finding that the effects of development on DOC export diminished as time progressed. He found that three years after clear-cutting, export was only 37 % greater than before deforestation whereas it was 190 % greater in the second year. In the present study, DOC export was 88 and 76 % of control levels five and two years respectively, after v-blading.

Although development did not greatly affect total amounts of runoff leaving the catchments during the 12 month study period, pathways of water entering streams were altered. L3 was much more responsive to rainfall than the other catchments (Jackson, 1987), and v-blade tracks rapidly transported water to the stream channel during storms. This runoff had little opportunity to pick up DOC from tracks or from the stream channel and was discharged from the catchment rapidly with little apparent net change in DOC concentration. At L1, however, retention of a relatively small area of manuka forest at the head of the catchment and growth of mosses in the stream channel appeared to mitigate some of the effects of v-blading on DOC dynamics. The increase in DOC export with time after development can be seen, in part, as steps in catchment succession following deforestation and indicate that, with the retention of an upstream buffer zone, DOC dynamics can approach pre-disturbance levels within five years.

CHAPTER 4

CHEMISTRY OF WESTLAND STREAMS

4.1. INTRODUCTION

Several workers have found strong relationships between the chemical nature of stream water and distributions of benthic invertebrates (e.g., Egglishaw & Morgan, 1965; Minshall & Minshall, 1978). Studies into the acidification of freshwater ecosystems by acid rain have highlighted the deleterious effects of low pH and its associated chemistry on aquatic life in the Northern Hemisphere (see Haines, 1981 and Dillon *et al.*, 1984). A major consequence of acidification in many streams has been the mobilisation of toxic aluminium (Al) species into the water column at concentrations which have proved fatal to many fish species. Labile (inorganic) monomeric Al is generally the toxic fraction whereas organically bound Al is essentially non-toxic (Driscoll *et al.*, 1980; Odonnell *et al.*, 1984). Concentrations of inorganic monomeric Al greater than 100-200 $mg.m^{-3}$ are considered lethal to many fish species (Baker & Schofield, 1982; Mason & Seip, 1985), but data on other animals are limited.

A survey of streams and rivers on the west coast of New Zealand's South Island showed that many had low pH (often < 5) and high concentrations of total Al (Winterbourn & Collier, 1987). Indeed, the most acidic and Al-rich streams drained catchments L1, L2 and L3 (Sites 2, d and e in Winterbourn & Collier (1987)) where annual DOC export ($g.m^{-2}$ of catchment area) is amongst the highest recorded in the world (see previous chapter). In the present chapter, I discuss further work on the interrelationships of several chemical variables (pH, alkalinity, DOC, conductivity and aluminium) at stream sites in North and South Westland, and report on the speciation of aluminium in some of these waters. The 29 North Westland sites were on streams draining the Larry River and Craigieburn pakihi terraces (see Fig. 2.2.), large areas of which have been developed by v-blading since the 1970s. In the South Westland part of the study, five streams (Sites 29, 30, 31, 33 and 34 of Winterbourn & Collier (1987)) draining undeveloped catchments (see Fig. 2.3.) were sampled bimonthly for one year to determine any seasonal variations in water chemistry.

4.2. METHODS

4.2.1. Sampling Protocol

Field surveys of the North Westland sites were undertaken in November 1986 and May 1987. Water samples (250 m*l*) were collected for chemical analysis and spot water temperatures were recorded on both dates. Streambed stability (see Pfankuch, 1975) and channel width were measured in May only. Aliquots of water (25 m*l*) for analysis of total reactive Al were collected concurrently with other water samples from all North Westland sites except L1, L2 and L3 where 1.85 *l* samples were taken for fractionation of Al. Sites 1-20 and L1-L7 were sampled on both occasions whereas Sites 21, 22 and 23 were sampled in May only. Sampling in November was preceded by a 26 day period with little rainfall (7.3 cm at LREA) and consequently discharges were much lower than in May.

Water samples for general chemical analysis (1 *l*) and fractionation of Al (1.85 *l*) were collected from the five South Westland streams on six occasions, at approximately two-monthly intervals between March 1985 and February 1986. Stream discharges and water temperatures were measured concurrently. Brownwater and clearwater streams were usually sampled on consecutive days.

4.2.2. General Chemical Analyses

All water samples were collected in opaque, polyethylene bottles and stored in the dark at 5^{o}C until analysis could be undertaken. Water pH was measured within six hours of sample collection with a Metrohm E488 meter (South Westland sites) or within two days with a Metrohm E512 meter (North Westland sites). Readings with the latter meter compared favourably (mean difference = 0.16 pH units, maximum = 0.6) with in-stream measurements obtained from 21 sites in the May survey using a Jenway 3060 portable pH stick, indicating that the two day interval between collection and measurement had little effect on pH. All meters were fitted with glass electrodes and were standardised immediately prior to use with pH 4 and pH 7 buffer solutions.

Other chemical analyses were carried out within a week of sample collection except that the September samples from South Westland were

frozen for four weeks before analysis. Conductivity was measured with a Radiometer CDM 2E meter and readings were converted to equivalent values at 25°C using the appropriate conversion factors in Table 3.1. of Golterman (1969). Alkalinity was determined in 50 m*l* (North Westland) or 100 m*l* (South Westland) aliquots of water by titration with 0.025 N HCl to pH 4.5 (Mackereth, 1963). DOC concentration was measured on filtered (0.45 μm) subsamples of water (25, 50 or 100 m*l*, depending on suspected concentration) using the heat-by-dilution dichromate oxidation procedure described in Section 3.2.1.

4.2.3. Aluminium Analyses

Fractionation procedure

Three fractions of aqueous Al were extracted and measured (see below for methodology): total reactive Al, total monomeric Al and labile monomeric Al. The difference between total monomeric Al and labile monomeric Al gives a measure of non-labile monomeric Al, and the difference between total reactive Al and total monomeric Al represents acid-soluble Al (Fig. 4.1.). Labile monomeric Al is comprised of free aquo-Al as well as inorganic complexes whereas non-labile monomeric Al is thought to consist predominantly of monomeric alumino-organic complexes (Driscoll, 1984). Acid-soluble Al is believed to include colloidal Al and extremely non-labile organic complexes.

All Al fractions were determined from a single volume of water removed from the stream at any one time. Total reactive Al was measured on subsamples of water (5 or 10 m*l*) which had been filtered (0.45 μm) on site using a Millipore apparatus and acidified to pH 1-2 with concentrated nitric acid. Acidification is believed to convert less reactive forms of Al, such as colloidal Al and strongly bound alumino-organic complexes, to faster reacting forms (Barnes, 1975). However, opinions differ regarding the length of time required before conversion is complete. Barnes (1975) recommended that acidified solutions should be kept for two weeks before extraction, but other workers including Driscoll (1984) and Seip *et al.* (1984) have used much shorter periods (1 hour and 24 hours, respectively). In the present study, acidified solutions were allowed to stand for at least three days before total reactive Al was extracted.

Total monomeric Al was extracted in the field immediately after water samples (5-10 m*l*) had been collected and filtered (0.45 μm). Several

methods have been used to separate labile and non-labile monomeric Al fractions, but the most widely used technique employs a cation exchange resin which adsorbs the labile monomeric fraction as the water sample passes through the exchange column; concentrations of this fraction are calculated by difference between total monomeric Al and non-labile monomeric Al which passes through the exchanger (Driscoll, 1984). This technique has a number of drawbacks, however, a major problem being that sample pH may be altered during passage through the column if the ionic strengths of the sample and exchange resin differ (Driscoll, 1984). For this reason, I concluded that the column method should not be used for making comparative analyses of water samples whose pH and ionic strength were likely to vary within and between sites.

LaZerte (1984) described an alternative method of separating labile and non-labile monomeric Al by equilibrium dialysis with Spectropor 6, 1000 mwt cut-off, dialysis tubing. Although he suggested that small Al-fulvic acid complexes (< 1000 mwt) may be able to penetrate the dialysis tubing, Lalande & Hendershot (1986) found that this technique clearly differentiated between monomeric fractions in water containing fulvic acid and leaf litter leachate. The equilibrium dialysis method was used to separate the labile and non-labile monomeric Al fractions in the present study. Dialysis was started soon after sample collection except on two occasions (March and May 1985; South Westland sites) when water was frozen until the dialysis tubing became available. Tubing was filled with deionised water and placed in 1.85 *l* containers of sample water at 20°C for 24 hours (LaZerte, 1984) after which aliquots (10 m*l*) of dialysate were extracted.

Extraction procedure

Aluminium was extracted from water samples using the procedure of Barnes (1975) as modified by LaZerte (1984) to enable extraction from small sample volumes. Duplicate extracts were taken from all South Westland samples and from Sites L1, L2 and L3; single extracts were taken from all other samples.

The oxine reagent of Barnes (300 μl) forms complexes with reactive Al and was mixed with filtered (0.45 μm) aliquots (5 or 10 m*l*) of water containing 2-3 drops of Phenol Red, a pH indicator. The pH of the solution was adjusted to 8.3 by dropwise addition of 5 M ammonium hydroxide (correct pH indicated by a red colour change) to minimise interference from organics and to eliminate fluoride complexing of monomeric Al (Barnes, 1975; May *et al.*, 1979). Finally, 300 μl of Barnes' buffer and 5 m*l* of

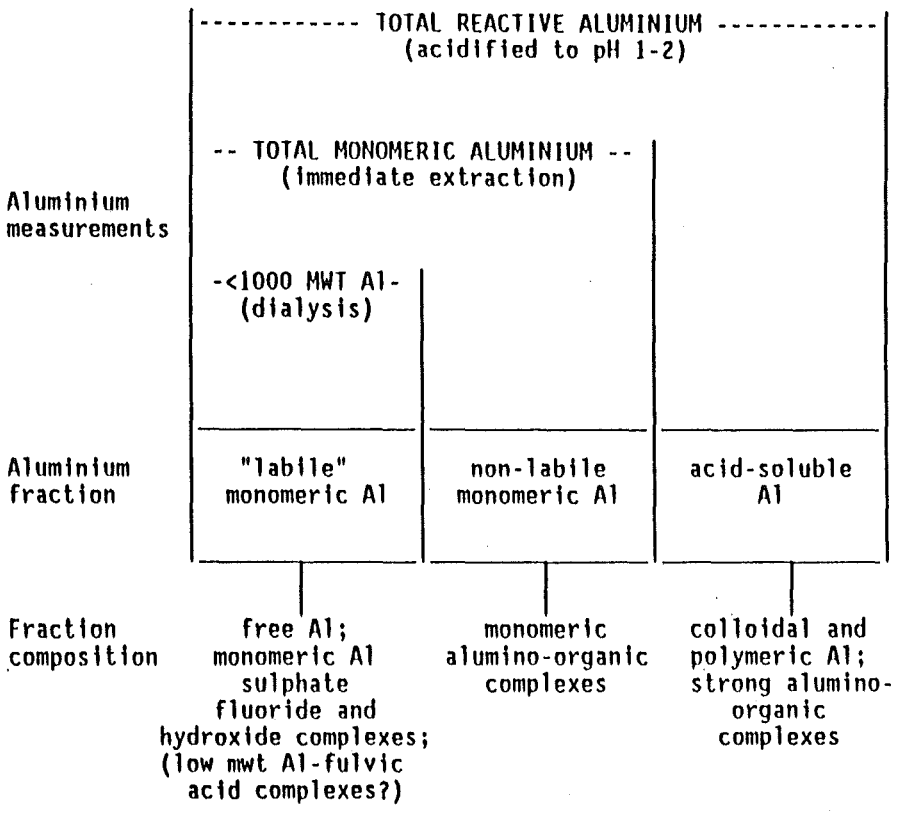


Figure 4.1. A schematic representation of the aluminium (Al) fractionation procedure used in this study (adapted from Driscoll, 1984).

Table 4.1. Carbon rod atomiser (C.R. 60) settings used for analysing aluminium in 10 μl aliquots of MIBK extract by flameless atomic absorption spectroscopy (Varian Techtron). Settings were obtained from Culver (1975) and were checked by continuously measuring absorbance patterns on a chart recorder.

Phase	Voltage	Time (seconds)
DRY	3.5	55
ASH	5.0	15
ATOMISE	8.0	3

methylisobutylketone (MIBK) were added to the solution which was shaken vigorously for 15 seconds. The mixture was allowed to separate and the upper phase (MIBK extract) was collected and stored in a freezer prior to analysis by flameless atomic absorption spectroscopy (FAAS).

Extract analysis and laboratory practices

FAAS was done on a Varian Techtron Model 1200 atomic absorption spectrophotometer equipped with a Model 63 carbon rod atomiser set as shown in Table 4.1. Ten microlitres of MIBK extract were injected into carbon tubes during the drying phase with a 701-N Hamilton syringe.

Extracts from the South Westland samples and those from Sites L1, L2 and L3 were analysed in triplicate; all others were done in duplicate. The mean coefficient of variation for 100 samples (two extractions each analysed three times) was 13.0 %. Standards (range 0-1000 $mg.m^{-3}$ Al) were prepared as described by Barnes (1975) and were stored in polyethylene bottles until required (within two weeks). They were extracted under the same conditions (field or laboratory) and with the same chemicals used for streamwater extractions, and were run routinely during FAAS.

All labware used for fractionation and extraction of Al had been soaked for at least 24 hours in 1 % nitric acid and washed twice in double distilled, deionised water. Dialysis tubing was stored in 1 % nitric acid, and before use, was given two 24 hour soakings in fresh acid before being washed thoroughly in high purity water (LaZerte, 1984). Disposable Med-X gloves were worn whenever dialysis tubing was handled. Fresh reagents and standards were made up prior to each sampling trip using high purity chemicals and water.

4.2.4. Physical Measurements

Maximum-minimum water temperatures were recorded at the five South Westland sites with thermometers kept submerged close to the stream bottom in commercial onion sacks anchored with heavy rocks and secured to nearby trees. Thermometers were read and reset on each sampling day.

Discharge of the South Westland streams was estimated by measuring the average time (three trials) taken for a cork to travel a known length of stream (1-5 m) and multiplying this by mean stream cross-sectional area determined at three points.

4.3. RESULTS

4.3.1. North Westland Sites

General water chemistry

DOC concentrations at the 29 sites surveyed ranged from 2.7 to 37.2 $g.m^{-3}$ and were higher in May than November at 23 of the 26 sites sampled twice (mean difference = 6.2 $g.m^{-3}$, maximum = 16.9 $g.m^{-3}$; Table 4.2.). Nevertheless, the rank order of DOC values was almost the same between surveys (r_S = 0.88). Lowest DOC concentrations (< 5.6 $g.m^{-3}$) in both surveys were recorded at Sites 9 and 12, clearwater streams originating in hills above the Craigieburn pakihi (Fig. 2.2.). Streamwater pH was also highest at these sites (> 6.4) in both surveys. At most other sites, pH was less than 6.0 and a minimum of 4.1 was recorded for three pakihi terrace streams in May (Sites 16, 17 and L1; Table 4.2.). Streamwater pH differed by an average of 0.4 units (maximum difference = 1.1 units) between surveys, but as with DOC, the rank order of sites was almost the same (r_S = 0.89).

All North Westland sites had low alkalinity and conductivity (< 6.4 $g.m^{-3}$ $CaCO_3$ and < 5.0 $mS.m^{-1}$, respectively; Table 4.2.). In the May survey, 14 sites had no measurable alkalinity whereas only seven had zero alkalinity in the November survey. Conductivity was lowest on both dates at Sites 13 and 14, pakihi terrace streams bordered by *Pinus radiata* and *Pseudotsuga* sp. trees, and highest in streams draining the upper terrace of the Larry River pakihi (Sites L1, L2 and L3). All chemical parameters were intercorrelated strongly ($P < 0.001$) except for conductivity which showed weaker associations (Table 4.3.). DOC was correlated significantly and negatively with pH and alkalinity but positively with conductivity.

Aluminium chemistry

Total reactive Al concentration ranged from 48 to 911 $mg.m^{-3}$ in November, but in May the maximum concentration recorded was much lower (539 $mg.m^{-3}$). This was despite Al concentrations being higher in May at 18 of the 26 sites sampled twice (Table 4.2.). In both surveys, concentrations were lowest (< 100 $mg.m^{-3}$ Al) in two circumneutral, clearwater streams (Sites 9 and 12), whereas levels were highest in November at Sites 8 and L5, both acidic, brownwater streams draining pakihi catchments. Total reactive Al was correlated significantly and positively with DOC but negatively with pH and alkalinity (Table 4.3.).

Concentrations of labile monomeric Al at Sites L1, L2 and L3 ranged from 19 to 76 $mg.m^{-3}$ in November when stream discharges were very low, and from 55 to 58 $mg.m^{-3}$ in May when flows were up to two orders of magnitude higher (Fig. 4.2.). In November, measured amounts of Al in total monomeric extracts exceeded those of total reactive Al at two of the three sites, indicating that the total monomeric fraction had become contaminated, probably during field extractions. In contrast, 38-63 % of total reactive Al was in the monomeric (labile + non-labile) form in May when acid-soluble Al concentrations were between 125 and 204 $mg.m^{-3}$. Concentrations of non-labile monomeric Al were less than 155 $mg.m^{-3}$ in May (Fig. 4.2.).

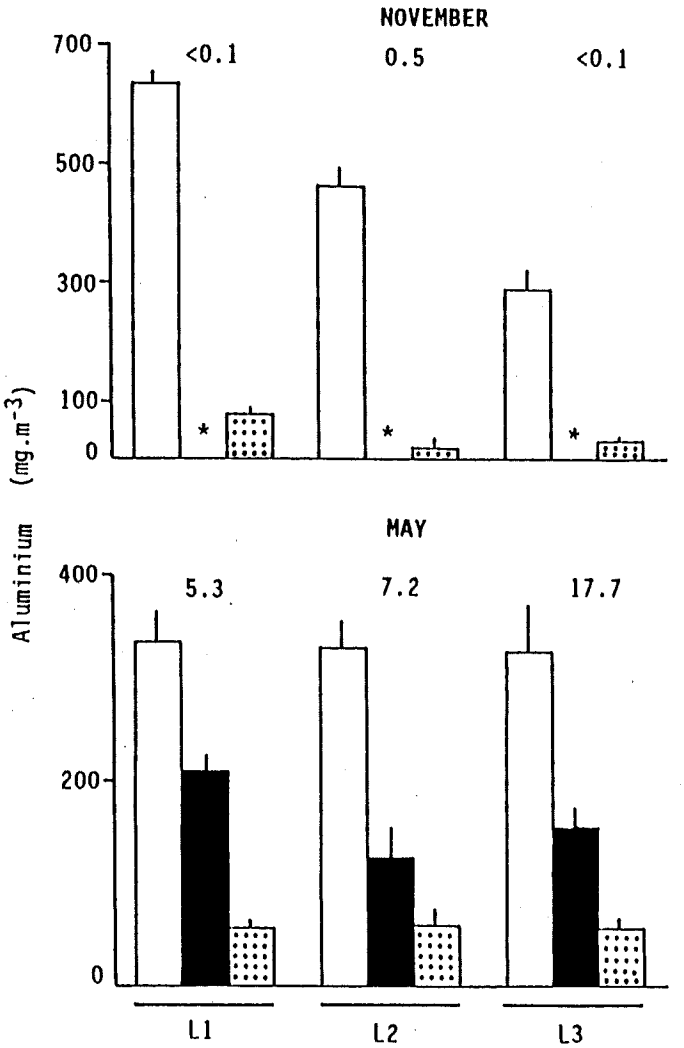


Figure 4.2. Concentrations ($\bar{x}$ + 2 SE, n = 6) of total reactive aluminium (open bars), total monomeric aluminium (closed bars) and labile monomeric aluminium (stippled bars) in water samples collected from sites L1, L2 and L3 (North Westland) in November 1986 and May 1987. Stream discharges ($l.s^{-1}$) at the time of sampling are given above histograms. *, samples contaminated.

Table 4.2. Water temperatures and chemical data from the 29 North Westland sites sampled in November 1986 (N) and May 1987 (M). -, not sampled; *, no data.

Site	Water temperature (°C)		pH		Alkalinity ($g.m^{-3} CaCO_3$)		DOC ($g.m^{-3}$)		Conductivity ($mS.m^{-1}$)		Total reactive Al ($mg.m^{-3}$)	
	N	M	N	M	N	M	N	M	N	M	N	M
1	14	10	6.0	5.2	3.8	1.3	7.8	17.4	*	2.7	135	386
2	16	10	6.1	5.4	4.1	1.6	11.1	20.1	3.4	3.0	206	443
3	19	10	6.3	6.3	5.0	3.4	5.7	11.9	3.4	2.9	127	331
4	24	9	4.7	4.8	0.9	0.3	13.2	14.8	2.1	2.3	172	393
5	15	10	4.8	4.8	0.9	0.3	10.5	11.7	1.9	2.1	223	450
6	19	10	4.7	4.7	0.6	0	10.2	13.3	1.8	2.2	228	465
7	25	10	4.6	4.6	0.3	0	15.6	18.8	2.0	2.2	453	394
8	22	11	4.7	4.5	0.3	0	18.6	22.5	2.9	3.1	911	493
9	15	10	6.5	6.5	5.3	5.0	2.9	5.2	3.4	3.1	48	97
10	23	12	4.5	4.4	0	0	11.3	22.9	3.4	3.0	663	321
11	21	12	4.8	4.6	0.3	0	7.2	11.7	2.3	2.3	286	420
12	11	9	6.6	6.5	6.3	4.4	2.7	5.5	3.1	3.0	50	91
13	27	11	5.2	4.7	0.9	0.6	5.7	11.3	1.6	2.0	117	331
14	25	11	5.1	4.7	1.3	0.3	7.3	11.6	1.6	2.0	141	439
15	16	10	5.9	4.8	2.2	0.6	10.8	17.3	2.4	2.2	188	329
16	22	10	4.4	4.1	0	0	22.8	24.6	3.3	3.0	346	346
17	25	11	4.4	4.1	0	0	20.4	29.4	3.1	3.6	304	271
19	15	10	5.6	4.6	2.5	0	16.5	25.7	3.2	2.8	252	449
20	11	9	6.6	6.1	*	2.2	*	10.2	*	2.1	149	210
21	-	10	-	5.8	-	1.6	-	15.4	-	2.6	-	329
22	-	10	-	6.0	-	2.2	-	15.7	-	2.6	-	329
23	-	10	-	4.6	-	0	-	20.2	-	2.7	-	470
L1	26	10	4.3	4.1	0	0	34.7	24.9	3.7	4.7	634	334
L2	13	9	4.2	4.2	0	0	37.2	20.3	4.4	4.6	461	328
L3	27	10	4.9	4.3	0.9	0	9.1	17.5	2.2	4.9	289	325
L4	31	14	4.6	4.2	0	0	21.8	29.4	3.2	3.9	524	530
L5	27	11	4.3	4.4	0	0	28.5	31.1	3.2	3.9	898	539
L6	16	10	6.4	5.4	4.1	1.3	9.6	18.4	2.9	2.3	171	325
L7	15	10	5.2	4.9	0.9	0.6	14.1	18.3	2.2	2.4	278	406

Table 4.3. Matrix of correlation coefficients between all physicochemical parameters measured at the North Westland sites in November 1986 and May 1987. Means of chemical parameters from both surveys and summer water temperatures (i.e., maxima) were used. All coefficients are for product moment correlations except for rank order of catchment development (Rank; see Table 2.1.) where Spearman correlations were calculated. Transformations were done on stream width, pH (both log (x)) and alkalinity (log (x+1)) to give best approximations to normality. *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$.

	Alkalinity	DOC	Conductivity	Total reactive Al	Channel width	Streambed stability	Temperature	Rank
pH	0.97***	-0.74***	-0.27	-0.71***	0.61***	0.17	-0.67***	-0.51**
Alkalinity		-0.71***	-0.17	-0.73***	0.63***	0.18	-0.66***	-0.50**
DOC			0.63***	0.74***	-0.53**	-0.14	0.41*	0.24
Conductivity				0.31	-0.36	0.21	0.11	0.07
Total reactive aluminium					-0.47*	-0.31	0.54**	0.54**
Channel width						-0.10	-0.40*	-0.45*
Streambed stability							0.25	0.11
Temperature								0.78***

Physical factors

Streamwater temperatures at the North Westland sites ranged from 11 to 31°C in the November survey and were highest in streams draining developed catchments of the Larry River pakihi (Table 4.2.). In the May survey, water temperatures were lower and fairly similar at all sites (range 9-14°C). Stream channel widths (Table 2.1.) ranged from 1 m at Sites L2 and L3 on the upper terrace of the Larry River pakihi to 24 m for Craigieburn Creek (Site 22) which receives most of the drainage from the Craigieburn pakihi.

Pfankuch (1975) streambed stability ratings which give more stable beds lower scores were highest (56) for Site L4 which drains a catchment developed in 1982-83, and lowest for three streams (Sites 5, 8 and 19) draining catchments on the Craigieburn pakihi (Table 2.1.).

At the North Westland sites, most of the chemical parameters measured were correlated significantly with physical aspects of the streams (Table 4.3.). The smallest streams (i.e., narrowest channel widths) tended to be more acidic and had higher DOC and total Al concentrations than larger sites. Streams draining more recently developed catchments tended to be the smaller ones and most had higher summer water temperatures than those draining undeveloped catchments. No chemical factors were correlated significantly with streambed stability.

4.3.2. South Westland Sites

General water chemistry

Water from Hidden Creek and Toilet Stream had the highest pH, alkalinity and conductivity, but the lowest DOC concentrations (Fig. 4.3.). Water pH was always above 7.0 and alkalinity above 41.4 $g.m^{-3}$ $CaCO_3$, except in September when pH in Hidden Creek was 6.6 and in May when alkalinity in Toilet Stream was 12.6 $g.m^{-3}$ $CaCO_3$. At the clearwater sites, the lowest conductivity reading (3.7 $mS.m^{-1}$) and the highest DOC value (4.7 $g.m^{-3}$) were recorded in May in Toilet Stream. On all other dates, conductivity in Hidden Creek and Toilet Stream ranged from 11.7 to 22.3 $mS.m^{-1}$ and DOC concentration was between 0.3 and 1.8 $g.m^{-3}$.

In water samples from Steep Creek and Suspect Stream, pH ranged from 4.3 to 5.7, alkalinity never exceeded 2.3 $g.m^{-3}$ $CaCO_3$, and conductivity was between 2.5 and 4.1 $mS.m^{-1}$. DOC concentrations were always high (> 6.5 $g.m^{-3}$) at these two brownwater sites with a maximum of 16.3 $g.m^{-3}$ recorded in January (Fig. 4.3.). Concentrations of DOC recorded on the six

dates were less variable in Steep Creek and Suspect Stream (CV = 30 and 22 %, respectively), than in Hidden Creek (CV = 50 %) or Toilet Stream (CV = 91 %), but alkalinity varied most at the two brownwater sites (Table 4.4.).

Chemical parameters in Mapourika Creek almost always fell between those of the other two pairs of sites on equivalent sampling dates (Fig. 4.3.). Mapourika Creek pH varied between 5.4 and 7.1, alkalinity and conductivity ranged from 2.7 to 23.0 $g.m^{-3}$ $CaCO_3$ and 2.1 to 7.9 $mS.m^{-1}$, respectively, and DOC concentrations never exceeded 8.4 $g.m^{-3}$. All measured chemical parameters including conductivity were intercorrelated strongly ($P < 0.001$) at the South Westland sites. DOC concentration was associated negatively with pH, alkalinity and conductivity (Table 4.5.).

Aluminium chemistry

Highest concentrations of total reactive Al and total monomeric Al were recorded in Suspect Stream (maxima 363 and 217 $mg.m^{-3}$, respectively), followed by Steep Creek and Mapourika Creek (Fig. 4.4.). In Hidden Creek and Toilet Stream, measured amounts of total reactive Al never exceeded 84 $mg.m^{-3}$ and monomeric Al was in the range 19-47 $mg.m^{-3}$. Labile monomeric Al concentrations were similar at all sites on equivalent sampling dates, but were always slightly higher in Steep Creek and Suspect Stream. Highest concentrations of this fraction were recorded in the September sample when values for all sites ranged from 36 to 50 $mg.m^{-3}$ (Fig. 4.4.).

A feature of the most acid streams (Steep Creek and Suspect Stream) was the large pool of non-labile monomeric Al (84-178 $mg.m^{-3}$) which was present on all sampling occasions (Fig. 4.4.). In contrast, concentrations of non-labile monomeric Al were more variable in Mapourika Creek (28-154 $mg.m^{-3}$), and never exceeded 33 $mg.m^{-3}$ in Hidden Creek or Toilet Stream. Acid-soluble Al concentrations fluctuated between 31 and 168 $mg.m^{-3}$ in Steep Creek and Suspect Stream, and between 16 and 145 $mg.m^{-3}$ in Mapourika Creek. However, concentrations of acid-soluble Al were always less than 46 $mg.m^{-3}$ in Hidden Creek and Toilet Stream (Fig. 4.4.).

Coefficients of variation calculated for all Al fractions over the six dates ranged from 22 to 85 %, and for most fractions temporal variability was least at Suspect Stream (Table 4.4.). Except for labile monomeric Al, all fractions were intercorrelated strongly with each other and with other chemical parameters (Table 4.5.). All Al fractions were related inversely with pH, alkalinity and conductivity but positively with DOC. Significant ($P < 0.05$) correlations were found between labile monomeric Al and pH, alkalinity and total reactive Al.

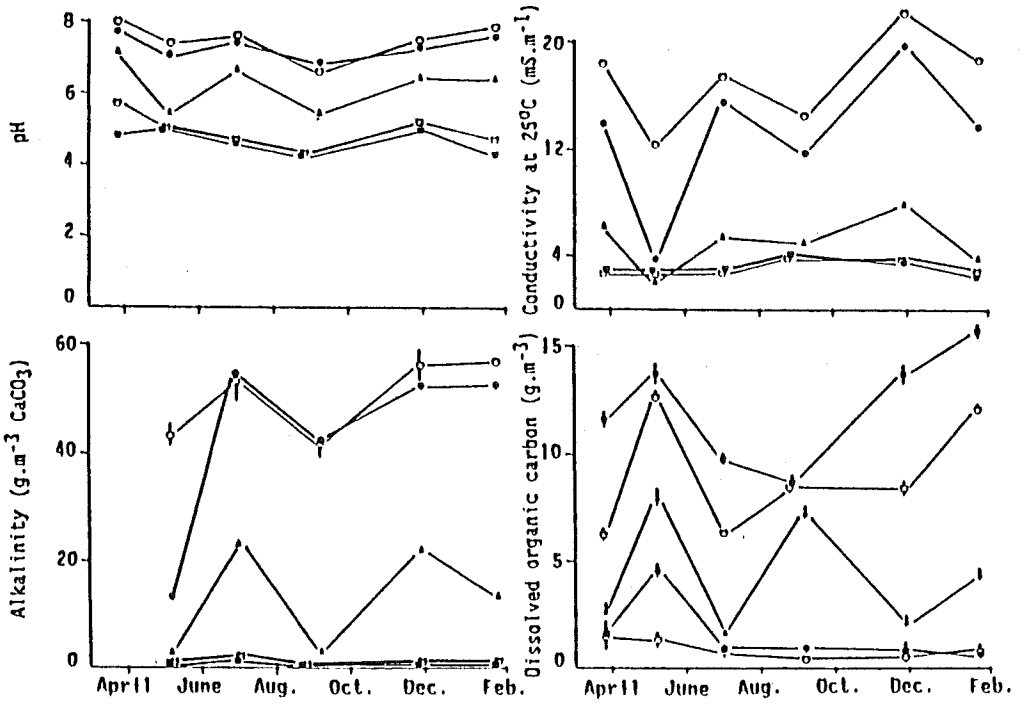


Figure 4.3. Chemical parameters measured on water samples taken from the five South Westland sites on six dates in 1985-86. Alkalinity and DOC, $\bar{x} \pm 2$ SE, n = 5; pH and conductivity, single readings. Error bars are not shown if accomodated within the symbol. ○, Hidden Creek; ●, Toilet Stream; ▲, Mapourika Creek; □, Steep Creek; ■, Suspect Stream.

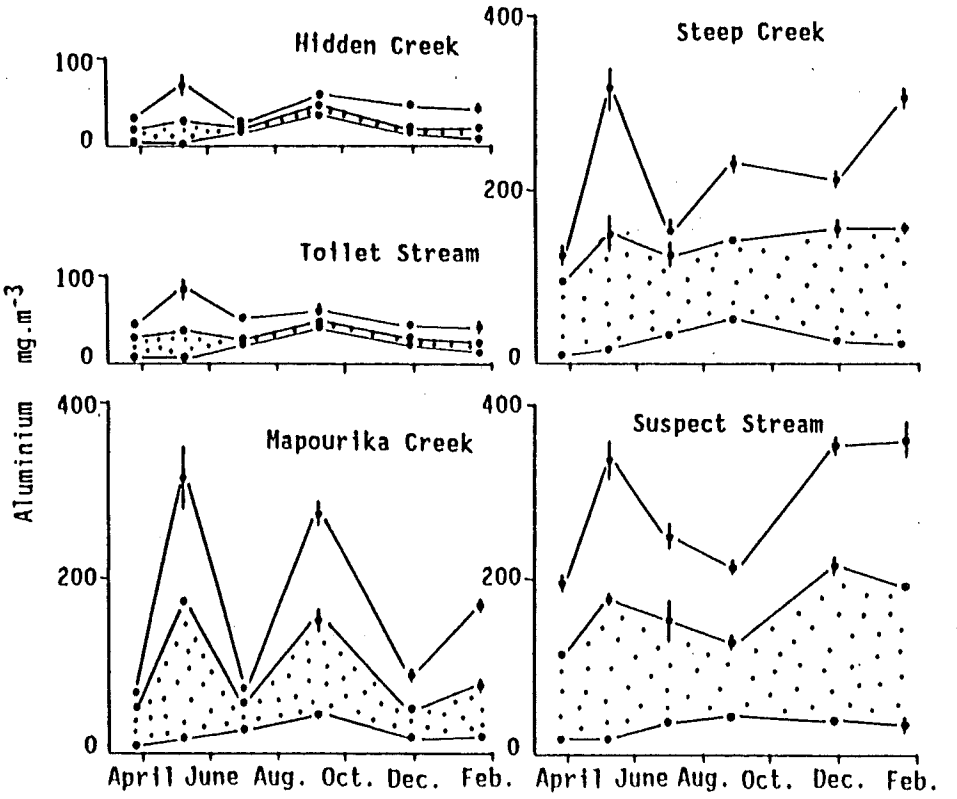


Figure 4.4 Concentrations ($\bar{x} \pm 2$ SE, n = 6) of total reactive aluminium (upper line), total monomeric aluminium (middle line) and labile monomeric aluminium (bottom line) measured in water samples from the five South Westland streams. The stippled area represents non-labile monomeric aluminium. Error bars are not shown if accomodated within the symbol.

Table 4.4. Coefficients of variation (%) calculated from the data obtained on six sampling dates for discharge and eight chemical parameters at the five South Westland sites.

Sites	Discharge	pH	Alkalinity	DOC	Conductivity	Total reactive Al	Acid-soluble Al	Non-labile monomeric Al	Labile monomeric Al
Hidden	66	7	15	50	20	35	64	67	84
Toilet	123	5	41	91	50	32	56	85	77
Mapourika	124	11	76	63	39	66	78	71	55
Steep	216	10	82	30	17	35	67	22	57
Suspect	223	7	139	22	19	26	32	29	36

Table 4.5. Matrix of product moment correlation coefficients between all chemical parameters measured in the five South Westland streams. All data were combined and log (x) transformed (alkalinity log (x+1) transformed). n = 30 except for alkalinity where n = 25. *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$.

	Alkalinity	DOC	Conductivity	Total reactive Al	Acid-soluble Al	Non-labile monomeric Al	Labile monomeric Al
pH	0.97***	-0.87***	0.85***	-0.91***	-0.80***	-0.83***	-0.64***
Alkalinity		-0.95***	0.89***	-0.94***	-0.85***	-0.91***	-0.47*
DOC			-0.92***	0.93***	0.88***	0.93***	0.30
Conductivity				-0.90***	-0.80***	-0.92***	-0.34
Total reactive Al					0.94***	0.93***	0.50**
Acid-soluble Al						0.86***	0.33
Non-labile monomeric Al							0.26

Physical factors

Water temperatures were relatively constant in spring-fed Hidden Creek throughout the study (range 8-12°C), but were more variable at the other sites where winter minima were 4-5°C and summer maxima ranged from 14 to 22°C (Table 4.6.). Hidden Creek also had a relatively stable flow regime (range when sampled 14-67 $l.s^{-1}$) compared with Toilet Stream (3-260 $l.s^{-1}$), Mapourika Creek (9-225 $l.s^{-1}$), and Steep Creek and Suspect Stream where flows were similar on equivalent sampling days (2-498 $l.s^{-1}$) (Table 4.7.). Although magnitudes of flow differed at the clearwater sites, both streams showed similar temporal patterns of discharge.

Water pH and alkalinity were correlated negatively with discharge at all sites whereas labile monomeric Al consistently showed positive (albeit sometimes weak) associations with discharge (Table 4.8.). Responses of other chemical parameters to flow varied depending on the stream. In Mapourika Creek most parameters were correlated strongly with discharge, but at the other sites only total reactive Al (Hidden Creek) and pH (Toilet Stream) were significantly correlated with discharge. When data from the clearwater streams were combined, discharge was correlated significantly with pH, alkalinity, total reactive Al and conductivity, but only with the latter variable when brownwater stream data were combined (Table 4.8.). Conductivity was correlated positively with discharge in the brownwater streams, whereas a negative relationship was found at the clearwater sites.

Table 4.6. Spot water temperatures and records from maximum-minimum thermometers (parentheses) from the five South Westland streams. Units are °C. -, no record.

	Sites				
Months	Hidden	Toilet	Mapourika	Steep	Suspect
March	12 (-)	13 (-)	12 (-)	12 (-)	12 (-)
May	11 (8-11)	10 (9-11)	11 (10-15)	12 (6-14)	12 (6-14)
July	11 (8-11)	7 (6-11)	8 (7-12)	8 (5-12)	7 (4-12)
Sept.	9 (8-12)	9 (6-11)	9 (7-10)	8 (5-9)	8 (-)
Nov.	10 (8-10)	14 (5-15)	12 (5-12)	13 (6-14)	13 (6-13)
Jan.	12 (-)	12 (9-17)	12 (11-22)	14 (-)	13 (11-17)
Annual range	8-12	5-17	5-22	5-14	4-17

Table 4.7. Discharges ($l.s^{-1}$; $\bar{x}$ (2 SE)) of the five South Westland study streams at times of sampling (n = 3).

Months	Sites				
	Hidden	Toilet	Mapourika	Steep	Suspect
March	14	3	9	4	2
	(3.2)	(0.4)	(1.0)	(1.6)	(0.6)
May	67	260	225	16	23
	(2.6)	(48.1)	(87.0)	(3.1)	(2.6)
July	14	11	19	4	7
	(3.7)	(1.6)	(3.6)	(2.2)	(2.3)
Sept.	46	181	217	498	494
	(16.5)	(10.5)	(84.6)	(27.1)	(55.6)
Nov.	29	33	16	2	3
	(7.8)	(6.0)	(4.4)	(0.6)	(1.6)
Jan.	20	32	24	30	4
	(14.8)	(5.0)	(8.4)	(12.0)	*

*, n = 1

Table 4.8. Product moment correlation coefficients for discharge and chemical parameters (both log (x) transformed; alkalinity log (x+1) transformed) measured in the five South Westland streams and for combined pairs of clearwater (Hidden Creek and Toilet Stream) and brownwater (Suspect Stream and Steep Creek) sites. n = 6 per site except for alkalinity where n = 5. *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$.

Sites	pH	Alk-alin-ity	DOC	Con-duct-ivity	Total react-ive Al	Acid-soluble Al	Non-labile monomer-ic Al	Labile mono-meric Al
Hidden	-0.67	-0.80	-0.27	-0.67	0.98***	0.62	0.54	0.01
Toilet	-0.87*	-0.77	0.32	-0.63	0.68	0.33	0.08	0.18
Mapourika	-0.98***	-0.99***	0.88*	-0.69	0.94**	0.83*	0.89*	0.60
Steep	-0.76	-0.78	0.36	0.60	0.45	0.54	-0.12	0.50
Suspect	-0.44	-0.52	-0.62	0.71	-0.26	-0.22	-0.49	0.32
Clear	-0.67*	-0.78**	0.19	-0.62*	0.67*	0.37	0.20	0.13
Brown	-0.56	-0.59	-0.09	0.65*	0.11	0.23	-0.33	0.38

4.4. DISCUSSION

Chemical composition of Westland stream water

Findings of this study confirm those of Winterbourn & Collier (1987) that brownwater streams in Westland are characterised by low pH, alkalinity and conductivity but high DOC and total Al concentrations. The variable responses of some chemical parameters to discharge (e.g., DOC, conductivity, Al) at the South Westland sites presumably reflect differences in hydrological pathways and residence times of rain water in soil profiles (see Bache, 1984). In South Westland, chemical parameters responded most predictably to changes in flow in Mapourika Creek which is bordered by free-draining, alluvial soils (N.Z. Soil Bureau, 1968). In contrast, soils in the head waters of Steep Creek and Suspect Stream are slowly-permeable gley podzols and hydrological pathways through these are likely to be different and partly dependent on antecedent weather conditions. The sampling site in Steep Creek was about 500 m from the the head waters where steep valley walls presumably contributed rapid runoff to the stream during storms. Water entering the clearwater streams in Franz Josef glacier valley was a mixture of spring water and runoff from rock surfaces and shallow soil horizons which are very well drained (pers. obs.; Stevens, 1968).

The chemical composition of water entering streams generally reflects the make up of the material through which it has passed (Bache, 1983). As precipitation percolates through or over soils, its composition is changed by relatively rapid cation exchange mechanisms and much slower acid hydrolysis reactions (Bache, 1984). The primary agent in hydrolysis is carbonic acid which is formed by the equilibration of atmospheric CO_2 in rain water; it decomposes primary minerals releasing ions (most often calcium and magnesium) into solution. This process consumes hydrogen ions thereby producing bicarbonate and elevating water pH, often to around pH 6-7 (Henriksen, 1981; Bache, 1984). Cation exchange in soils is almost exclusively a property of decayed organic matter and silicate minerals which have negative charges and thus adsorb a layer of cations (McFee *et al.*, 1971). Adsorbed cations can be interchanged with cations in soil water and this process can acidify or neutralise percolating water depending on the cations being exchanged (van Breeman *et al.*, 1984).

Hydrolysis is potentially the major process affecting the chemical composition of water draining into Hidden Creek and Toilet Stream where large amounts of undecomposed rock (mainly schists) are exposed and soil

horizons contain little organic matter (Stevens, 1968). These two streams had relatively high alkalinities (up to 57.6 $g.m^{-3}$ $CaCO_3$), partly reflecting the abundance of bicarbonate ions which are the main buffer in waters of circumneutral pH (Reynolds & Neal, 1987). However, in circumneutral streams in North Westland, alkalinity is low (< 6.4 $g.m^{-3}$ $CaCO_3$), perhaps because more of the runoff entering these streams is derived from the soil where much of the alkalinity could be neutralised by organic acids. Alkalinity values for acidic streams (pH < 6.0) should be treated with caution because the acidimetric titration method used can overestimate bicarbonate buffering capacity (Reynolds& Neal, 1987).

Nevertheless, the low conductivities of the North Westland sites, and the relatively high values obtained for the South Westland clearwater streams may partly reflect abundance of the bicarbonate ion. This is supported by the strong correlation between alkalinity and conductivity for the South Westland sites. The poor correlations between conductivity and most chemical parameters at the North Westland sites probably reflect the relatively narrow range of conductivities recorded there (1.6-4.9 $mS.m^{-1}$) compared with the South Westland sites (2.5-22.3 $mS.m^{-1}$). Conductivity decreased with increasing discharge in the South Westland clearwater streams, indicating that free ion concentrations were highest during base flow conditions and presumably were diluted by rainfall. In contrast, a significant positive relationship between conductivity and discharge was found when data from the two brownwater sites were combined, suggesting that ions were mobilised into the stream water at higher flows. This differs from the findings of Pearce & Griffiths (1980) who reported no difference in conductivity or pH during storm flow in a brownwater stream in nearby Okarito Forest. Reasons for these contrasting results are unclear.

Most water entering stream channels from pakihis moves laterally through upper soil horizons or surface vegetation (Jackson, 1987; Mew & Lee, in press) and thus would be expected to make less contact with primary minerals than runoff entering glacial valley streams. In pakihi soils, cation exchange is likely to be the dominant process affecting the composition of water entering streams. Cation exchange in concert with organic acid production by microbial decomposition of organic matter, acidifies the water and lowers its ionic content (Thurman, 1985) causing low conductivity. The importance of organic acids in regulating the acidity of brownwater streams is evidenced by the strong inverse correlation detected between DOC concentration and pH for both North and South Westland data sets. Both the pH and alkalinity of stream water fell as flows increased at all South

Westland sites. Reid *et al.* (1981) also observed this relationship and a corresponding rise in organic carbon concentration in a river draining a moorland catchment in Scotland, and suggested that more water flowed through the upper organic layers during storms. DOC concentration was positively correlated with discharge in Toilet Stream, Steep Creek and Mapourika Creek, but the correlation was statistically significant only at the latter site.

Concentrations and sources of aluminium

Because of relatively low solubility of Al in the pH range 5-9, concentrations of this element in most natural waters are low and values considerably less than 1 $mg.m^{-3}$ have been reported (Odonnell *et al.*, 1984). At pH values above 9 and below 5, Al dissolves readily in water and its solubility can be enhanced greatly (up to 100 times) by the presence of organic ligands (Cronan & Schofield, 1979; Odonnell *et al.*, 1984). Some of the highest concentrations of total Al recorded in fresh waters (810 $g.m^{-3}$) were found in ponds acidified to pH < 2 by fumigations from spontaneously burning bituminous deposits in northwestern Canada (Havas & Hutchinson, 1983).

Total Al concentrations measured in Westland streams ranged from 27 $mg.m^{-3}$ in Hidden Creek to 911 $mg.m^{-3}$ in a pakihi stream on the Craigieburn terrace. The latter value is less than the maximum of 1200 $mg.m^{-3}$ reported by Otto & Svensson (1983) for acid, brownwater streams in southern Sweden, but more than the 790 $mg.m^{-3}$ recorded by Verry (1975) in Minnesota bog waters. The maximum total Al concentration reported by Winterbourn & Collier (1987) for West Coast waters was 697 $mg.m^{-3}$ at Site L1 in LREA.

Most Al in stream water is thought to originate in the surrounding terrestrial ecosystem (Johnson *et al.*, 1981; Hendershot *et al.*, 1984), although experimental additions of acid to streams have shown that some Al can be mobilised from streambed sediments (Hall *et al.*, 1980). The capacity of DOC to bind with metals such as Al is well known (Reuter & Perdue, 1977; Hart, 1981; Rate, 1987), and much of the complexation in soils apparently occurs by cation exchange as organic acids are leached from surface humic layers and drain through mineral subsoils. The translocation of Al as organo-metallic complexes from mineral A horizons and its subsequent precipitation in less acid B horizons is believed to contribute to the formation of some podzols (Thurman, 1985; Farmer, 1986). Deposition of sulphate and nitrate in acid rain is believed to have lowered the pH of some

Northern Hemisphere podzol B horizons thereby reducing precipitation of Al which can then pass as inorganic complexes to lakes and streams (Cronan & Schofield, 1979; Reuss *et al.*, 1987).

Because most of the water draining undisturbed pakihi soils does not contact B horizons but moves laterally through surface vegetation and upper soils layers, most Al entering these streams is likely to be organically bound. Although Ross *et al.* (1977) found that total Al accounted for less than 2 % of A horizon dry weight in Okarito soils, exchangeable Al dominates the cation exchange complexes of these soils (Mew & Lee, 1981). Additional Al could be generated in upper soil horizons adjacent to some brownwater streams through plant uptake from lower horizons and wind blown dust, especially that generated by v-blading. Sparling (1967) suggested that the main source of Al in British and Irish bogs was dust from exposed rocks, bare ground and roads, whereas Turner *et al.* (1985) found that considerable amounts of Al were cycled between mineral soils and the forest floor by vegetation in a watershed on the New Jersey Pine Barrens.

Fractionation of aluminium in Westland streams

Several workers have reported strong positive correlations between DOC and total Al concentration in brown waters (e.g., Otto & Svensson, 1983; Turner *et al.*, 1985; Clair & Freedman, 1986) and this suggests that most Al in humic waters occurs as organic complexes. This hypothesis was supported in the present study by the highly significant correlations detected between DOC and total Al, non-labile monomeric Al and acid-soluble Al, although the latter correlation may indicate greater concentrations of colloidal Al (< 0.45 μm) at the South Westland brownwater sites.

Fractionation of Al in water samples collected on six dates from Steep Creek and Suspect Stream, South Westland showed that, on average, non-labile monomeric Al comprised 49 % and acid soluble Al 39 % of the total. In May 1987 at Sites L1, L2 and L3, these fractions respectively, constituted 32 % and 51 % of total Al. The sum of non-labile monomeric and acid-soluble Al measured at brownwater sites in Westland (83-88 %) falls within the range of organically bound Al (80-90 %) found in some North American bog waters (Helmer, 1987; cited in Urban *et al.*, 1987).

Concentrations of toxic labile monomeric Al were low at all sites (< 80 $mg.m^{-3}$) and overall this fraction represented only 12 % (Steep Creek and Suspect Stream) and 17 % (Sites L1, L2 and L3) of total Al in brownwater streams. LaZerte (1984) also used the dialysis technique to measure labile monomeric Al in some organically-coloured Canadian waters and found that

concentrations normally were below 100 $mg.m^{-3}$, although a maximum of 175 $mg.m^{-3}$ was detected during peak discharge. In contrast, labile monomeric Al is the dominant fraction in many Northern Hemisphere clearwater streams acidified by acid rain, and concentrations as high as 600 $mg.m^{-3}$ have been reported (Seip *et al.*, 1984; Bull & Hall, 1986).

As the pH of water drops below about 4.5, complexation of Al with organic matter is believed to decrease dramatically and an increase in concentration of inorganic ions results (Krug & Frink, 1983; Mason & Seip, 1985). This process may have been important in regulating labile monomeric Al concentrations in South Westland streams where a highly significant inverse correlation was detected with pH but not DOC. However, even though pH as low as 4.1 was recorded at Site L1, this process did not elevate labile monomeric Al concentrations above 76 $mg.m^{-3}$.

Effects of catchment development on streamwater acidity

Afforestation is known to acidify soils through the uptake of base cations and their subsequent export from catchments after logging, but the effects of this on streamwater acidity have yet to be established beyond doubt (Harriman & Wells, 1985). Some workers have suggested that afforestation is likely to acidify surface waters only if mobile anions such as sulphate and organics are present to transfer the acidity to drainage waters (Nilsson *et al.*, 1982; Reuss *et al.*, 1987). During natural forest growth, acidification of soils due to excess uptake of base cations is essentially balanced by neutralising processes resulting from mineralisation of the organic litter layer (Harriman & Wells, 1985).

In the North Westland streams, a significant negative correlation was found between pH of water and rank order of development; i.e., streams draining more recently developed catchments were, in general, more acidic than streams draining undisturbed or less recently developed catchments. Although logging of the Larry River and Craigieburn terrace forests prior to their conversion to pakihi (Washbourn, 1972; Jackson, 1987) presumably resulted in the export of base cations from these catchments, it seems unlikely that this would have lowered water pH significantly because even streams draining native forest catchments can have pH as low as 4.1, the minimum recorded during the study (e.g., Site 16).

A stronger correlation was detected between stream size (width) and pH suggesting that streams draining developed catchments were more acidic because their head waters were closer to the pakihi source where large amounts of DOC (and by implication organic acids) can be generated within

soil horizons (see Chapter 3). In developed catchments, oxidation of sulphur to sulphate as soils dry out after drainage can be another source of acidity affecting streams (Bache, 1984; Stoner *et al.*, 1984). However, because Site L2 (undeveloped pakihi) had slightly lower pH than most recently-developed sites nearby, sulphur oxidation is unlikely to have had a major effect on streamwater pH.

Lawrence *et al.* (1987) found that concentrations of labile (inorganic) monomeric Al increased to potentially toxic levels following harvesting of trees from a watershed in Hubbard Brook Experimental Forest. At Sites L1, L2 and L3, concentrations of labile monomeric Al were similar and relatively low, indicating that development of pakihi catchments did not alter toxic Al levels significantly.

CHAPTER 5

EFFECTS OF pH AND CATCHMENT DEVELOPMENT ON THE DISTRIBUTION OF BENTHIC INVERTEBRATES IN NORTH WESTLAND STREAMS

5.1. INTRODUCTION

Many surveys of Northern Hemisphere streams have implicated pH of the water as a primary factor limiting the distribution of benthic invertebrates (e.g., Townsend *et al.*, 1983; Weatherley & Ormerod, 1987). In southern Sweden, Otto & Svensson (1983) found about half as many species (20-25) in streams with pH 5.0-5.5 as in less acidic streams (pH 6.0-6.5), and reported significant correlations between water pH and numbers of grazer and shredder species. Sutcliffe & Carrick (1973) discovered that, at pH < 5.7, mayflies and many caddisfly species were absent from the River Duddon and its tributaries where faunas were dominated by stoneflies. A similar observation was made by Simpson *et al.* (1985) for acid streams (pH 4.4-5.0) in the Adirondack Mountains, New York, and experimental studies have indicated that mayflies in general are particularly sensitive to acidification (Bell & Nebeker, 1969; Fiance, 1978; Ormerod *et al.*, 1987).

In a survey of streams on the west coast of South Island, New Zealand, Winterbourn & Collier (1987) found that invertebrate species richness was not affected by water acidity until pH reached about 4.5, and that similar numbers of ephemeropteran, trichopteran and plecopteran taxa were represented in a wide range of brownwater streams above this pH. Because the proximity of sites appeared to be important in determining the composition of benthic assemblages in that study, I conducted a survey of streams in the confined localities of the Craigieburn and Larry River pakihi terraces (see Fig. 2.2.) to assess effects of water chemistry on invertebrate distributions. In addition, because many streams on the terraces drain catchments that have been developed for forestry to varying degrees, I was able to investigate possible effects of this on benthic communities. Thus, comparisons of invertebrate communities were made between streams draining undisturbed (native forested) and disturbed catchments, the latter being defined as those developed for forestry or those which originally were covered by native forest but now are induced pakihi.

5.2. METHODS

5.2.1. Benthic Invertebrate Sampling

Sample collection

Benthic macroinvertebrates were collected from stony areas in all North Westland study streams in November 1986 and May 1987. Collections were made by kicking the substrate vigorously and brushing the surfaces of displaced stones in front of a triangular net (1 mm mesh). An attempt was made to collect in as many stream microhabitats as possible and to sample all streams with similar effort on both dates. In the May survey, the 1 mm mesh net was used in tandem with a 0.2 mm mesh net to test the efficiency of the former in capturing representatives of all taxa. All benthic samples were preserved in the field with 70 % ethanol.

Enumeration and identification of invertebrates

Benthic samples collected with the 1 mm mesh net were placed in a white tray and picked through twice. Ten samples collected with the 0.2 mm mesh net in May were selected randomly and washed over 1 mm and 0.2 mm mesh sieves. Material collected on the latter sieve was subsampled with a quadripartite splitter and invertebrates in one subsample were identified and counted under a binocular microscope.

Identifications were made using keys published by McFarlane (1951), Chapman & Lewis (1976), Cowley (1978), Winterbourn & Gregson (1981), Towns (1983a), Ordish (1984) and McLellan (1987), and in most instances were to species or genera. Exceptions were oligochaetes and mites which were not differentiated beyond order or class, and Chironomidae which were not separated below family.

5.2.2. Statistical Analysis

Classification procedures

Data were analysed using two-way indicator species analysis (TWINSPAN; Hill, 1979a) with the *PC-ORD* multivariate statistics package (McCune, 1987). TWINSPAN is a polythetic (all "species" used), divisive method of heirarchical analysis which classifies both sites and species into groups of similar composition, and identifies "indicators" which are diagnostic of each division. Classifications were performed with invertebrate presence/absence data obtained from each survey (November 1986 and May 1987) and combined survey data.

Ordination procedure

Detrended correspondence analysis (DECORANA; Hill, 1979b) was used to investigate patterns of taxonomic similarity among the North Westland sites with the *PC-ORD* package. In DECORANA, sites are arranged in an objective order along axes so that taxonomically similar sites occur most closely together. An axis score is generated and can be used to relate the ordination to measured environmental variables. Strengths of axes are measured as eigenvalues and the relative importance of an axis in explaining the variation of a data set can be expressed as the eigenvalue divided by the sum of eigenvalues for all axes (Weatherley & Ormerod, 1987).

DECORANA was performed on presence/absence data obtained in each survey and both surveys combined. Three sites sampled in May but not November were excluded from ordination analyses to enable correlation of DECORANA axes with mean chemical data from both surveys.

Correlations with environmental variables

Principal component analysis (PCA), correlation coefficents and stepwise multiple regression (*STATISTIX*; NH Analytical Software) were used to identify which environmental variables (see Chapter 4) best explained the distribution of sites along the ordination axes generated by DECORANA. Averages of chemical parameters (pH, alkalinity, DOC, conductivity and total reactive Al) measured in both surveys, and summer (November) stream water temperatures were used in all calculations. Transformations were done on stream width, pH (both $\log(x)$) and alkalinity ($\log(x+1)$) to give best approximations to normality. PCA and correlation coefficients were used to aid selection of key environmental variables and

to minimise redundancy. After initial multiple regressions, redundant variables were eliminated and regression equations were calculated for interpretable axes using key variables only. Rank order of catchment development (see Table 2.1.) was not included in principal component or multiple regression analyses because it deviated considerably from a normal distribution.

Relationships between TWINSPAN site groups (both surveys combined) and key environmental variables were examined by stepwise multiple discriminant analysis (MDA) using *BMDP* (Dixon, 1981). The method assigns sites to pre-defined (TWINSPAN) groups on the basis of environmental data alone, and assesses how accurately key variables can predict site groupings.

5.3. RESULTS

5.3.1. Sampling Efficiency

In the May survey, a 0.2 mm mesh net was used in tandem with a 1 mm mesh net to determine the efficiency of the coarse mesh for capturing representatives of all taxa. A total of 22 taxa were taken with the fine mesh net and not the 1 mm mesh net from ten sites, but 13 of these taxa were collected with the coarse mesh net in November (Table 5.1.). Most "new taxa" were taken in low numbers, but mites (Acarina) were abundant at many sites.

Sampling with a 1 mm mesh net underestimated densities of many taxa. For example, very large numbers of small *Deleatidium* spp. larvae were collected in fine mesh samples from Sites 3, 15 and 21, and all *Spaniocercoides cowleyi* larvae collected at L2 in May passed through the 1 mm mesh (Table 5.1.). Similarly, chironomid densities were grossly underestimated at all sites using a 1 mm mesh net. Therefore I concluded that quantitative data should not be used for analyses of North Westland benthic communities, but that it was valid to use presence/absence data. Mites and unidentified hydrobiosids were omitted from all calculations.

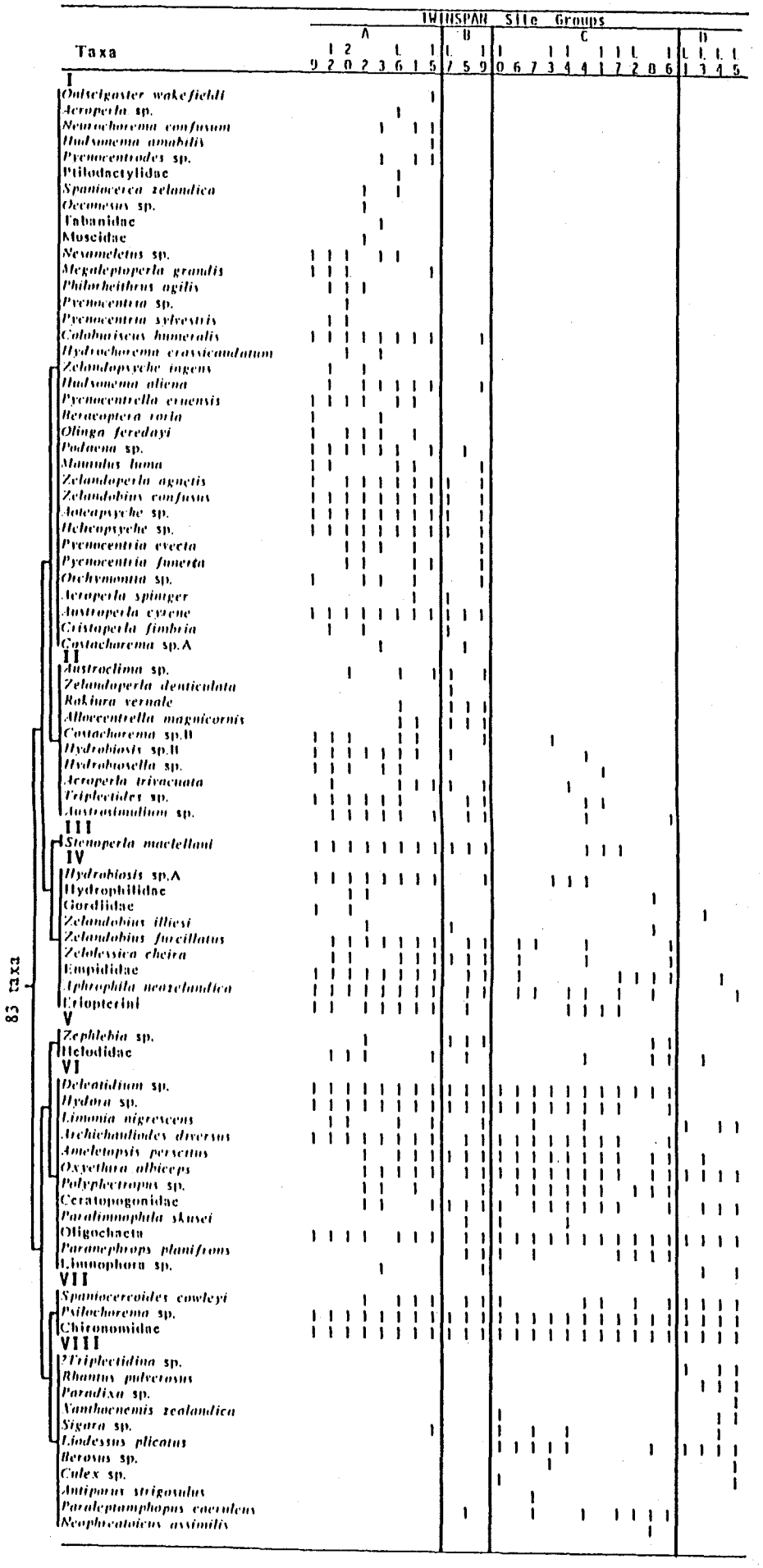
5.3.2. Taxonomic Richness

Altogether, 83 taxa were recognised in samples taken with a 1 mm mesh net from the 26 sites sampled twice (Table 5.2.); 72 in November and 74 in May. No taxa were confined to Sites 21, 22 or 23 which were sampled in May only. More taxa were recorded in May than November at 14 sites, but the mean difference in numbers per site between surveys was small (2.8 taxa). Ninty-four percent of taxa were insects with Trichoptera accounting for 38 % of these. Most taxa (43) were found at Site 2, a low terrace stream surrounded by native beech-podocarp forest. Sites 19, 20, 1, 3, 12, and 15 all realised 36-39 taxa, and all drained undisturbed, forested catchments around the Craigieburn pakihi. Fewest taxa were recorded from Sites L1 and L2 (8 and 9, respectively), which are acid, brownwater streams draining a high terrace pakihi in LREA.

Chironomids and the hydrobiosid caddis *Psilochorema* sp. were found at all 26 sites sampled twice, oligochaetes at 24, and *Deleatidium* spp.,

TRICHOPTERA										
Helicopsyche	0	28	40	0	0	0	12	20	0	168
sp.	(0)	(84)	(25)	(0)	(0)	(0)	(N)	(24)	(0)	(213)
Rakiura	0	4	0	0	0	0	0	0	0	0
vernale	(0)	(2)	(0)	(33)	(0)	(0)	(0)	(0)	(0)	(0)
Philorheithrus	0	0	0	0	0	0	4	0	0	0
agilis	(0)	(0)	(0)	(0)	(0)	(0)	(1)	(0)	(0)	(0)
Olinga	0	0	8	0	0	0	0	0	0	368
feredayi	(0)	(0)	(23)	(0)	(0)	(0)	(0)	(0)	(0)	(83)
Beraeoptera	0	0	20	0	0	0	0	0	0	0
roria	(0)	(0)	(N)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
Zelolessica	0	0	0	4	0	0	0	12	0	0
cheira	(0)	(11)	(0)	(53)	(0)	(0)	(7)	(N)	(8)	(0)
Pycnocentrella	0	4	0	0	0	0	0	0	0	0
eruensis	(0)	(1)	(0)	(0)	(0)	(0)	(4)	(0)	(0)	(0)
Pycnocentrodes	0	0	12	0	0	0	0	0	0	1132
sp.	(0)	(0)	(N)	(0)	(0)	(0)	(0)	(1)	(0)	(160)
Pycnocentria	0	0	0	0	0	0	0	0	0	128
evecta	(0)	(0)	(1)	(0)	(0)	(0)	(0)	(0)	(0)	(166)
Pycnocentria	0	0	0	0	0	0	12	0	0	0
sylvestris	(0)	(0)	(0)	(0)	(0)	(0)	(3)	(0)	(0)	(0)
Pycnocentria	0	0	0	0	0	0	0	20	0	0
funerea	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(2)	(0)	(0)
Aoteopsyche	0	4	4	0	0	0	0	0	0	12
sp.	(0)	(2)	(83)	(0)	(0)	(0)	(4)	(23)	(0)	(38)
Oxyethira	0	0	0	0	16	4	0	8	16	0
albiceps	(0)	(1)	(1)	(1)	(6)	(7)	(0)	(4)	(7)	(0)
Hydrobiosella	0	0	0	0	0	0	4	0	0	0
sp.	(0)	(0)	(1)	(0)	(0)	(0)	(1)	(0)	(0)	(0)
Polyplectropus	8	0	0	0	16	0	0	0	0	0
sp.	(N)	(0)	(0)	(0)	(3)	(2)	(0)	(0)	(0)	(0)
Psilochorema	20	0	4	28	0	0	0	0	16	16
sp.	(1)	(1)	(5)	(9)	(19)	(2)	(1)	(4)	(6)	(6)
Hydrobiosidae	4	36	76	0	24	0	12	40	0	84
indet.	(N)	(1)	(1)	(0)	(2)	(0)	(2)	(1)	(0)	(2)
COLEOPTERA										
Podaena	0	0	0	8	0	0	8	8	0	0
sp.	(0)	(1)	(1)	(5)	(0)	(0)	(6)	(1)	(0)	(0)
Orchymontia	0	0	0	0	0	0	0	0	0	24
sp.	(0)	(0)	(4)	(0)	(0)	(0)	(0)	(0)	(0)	(8)
Helodidae	0	0	0	0	0	4	0	0	8	0
	(0)	(0)	(0)	(2)	(0)	(4)	(4)	(1)	(3)	(0)
Hydora	0	4	176	16	0	0	124	52	0	232
sp.	(0)	(17)	(110)	(47)	(1)	(0)	(189)	(30)	(8)	(185)
Liodessus	0	0	0	0	32	20	0	0	0	0
plicatus	(0)	(0)	(0)	(0)	(N)	(N)	(0)	(0)	(0)	(0)
DIPTERA										
Chironomidae	384	131	812	168	700	120	132	276	560	260
	(4)	(9)	(28)	(217)	(13)	(14)	(12)	(22)	(28)	(33)
Austrosimulium	0	0	4	12	0	0	0	20	0	32
sp.	(0)	(2)	(1)	(N)	(0)	(0)	(1)	(12)	(1)	(2)
Ceratopogonidae	4	8	0	12	32	8	4	4	16	0
	(*)	(*)	(2)	(3)	(4)	(*)	(*)	(1)	(2)	(0)
Empididae	12	8	0	16	0	8	4	4	0	0
	(18)	(N)	(3)	(50)	(0)	(3)	(N)	(30)	(1)	(3)
Aphrophila	0	24	0	0	0	0	0	0	0	4
neozelandica	(0)	(70)	(7)	(14)	(1)	(0)	(3)	(7)	(0)	(2)
Tipulidae	4	0	0	0	0	0	0	0	0	0
indet.	(*)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)	(0)
Nothodixa	0	0	0	4	0	0	0	4	0	0
sp.	(0)	(0)	(0)	(*)	(0)	(0)	(0)	(*)	(0)	(0)

Table 5.2. Sites where macroinvertebrate taxa were found in combined surveys (November 1986 and May 1987) of 26 North Westland stream and river sites. TWINSPAN taxa groupings (I-VIII) are given on the left. 1 = present.



Oxyethira albiceps and *Hydora* sp. at 20-22. Forty-four taxa were recorded at less than six sites, but of them only *Megaleptoperla grandis*, *Baraeoptera roria*, *Olinga feredayi* and *Pycnocentria evecta* were abundant at any site (> 50 per two standard collections). The black amphipod, *Paraleptamphopus caeruleus*, was found at seven sites but was abundant only in cool streams draining undeveloped pakihi.

5.3.3. Classification

TWINSPAN site classifications were arrested at Level 2 beyond which groupings could not be interpreted by the environmental variables measured (discussed later). Four site groupings were generated at Level 2 using presence/absence data from November, May and combined surveys (Fig 5.1.). The initial separation at Level 1 can be interpreted as a distinction between very acidic (pH mostly < 5.0) sites draining disturbed catchments (Groups C and D) and less acidic streams (pH always > 4.5) draining mainly undisturbed catchments (Groups A and B). Only Site 16 which was forested with no upstream development evident was consistently misassigned on this basis. Of the three sites sampled in May only, two were assigned to TWINSPAN Group A (Sites 21 & 22 which receive most of the drainage from the Craigieburn pakihi) whereas the third, Site 23 drained an undisturbed catchment on the Craigieburn terrace, and was placed in Group B. Indicator species for undisturbed sites were the predatory stonefly, *Stenoperla maclellani* (November), a net-spinning caddisfly, *Aoteapsyche* sp. (May), and a detritivorous stonefly, *Austroperla cyrene* (both surveys combined) (Fig. 5.1.).

Group D consisted of streams draining recently developed (1980 or later) catchments of LREA, and was distinguished from Group C by the absence of *Deleatidium* spp. larvae (Fig. 5.1.). Group C contained the same sites in all classifications, but in May also included Site 5 which otherwise was assigned to Group B. Site L7 was always in Group B and Sites 3, 9, 12 and 20 were always in Group A. Overall, sites in Group B were distinguished from those in Group A by the presence of the mayfly *Zephlebia* sp. and the helicopsychid caddis, *Rakiura vernale*. In May, *Ameletopsis perscitus* and *Alloecentrella magnicornis* were the indicator species for Group B, whereas *Coloburiscus humeralis* distinguished Group A from Group B in the November survey (Fig. 5.1.).

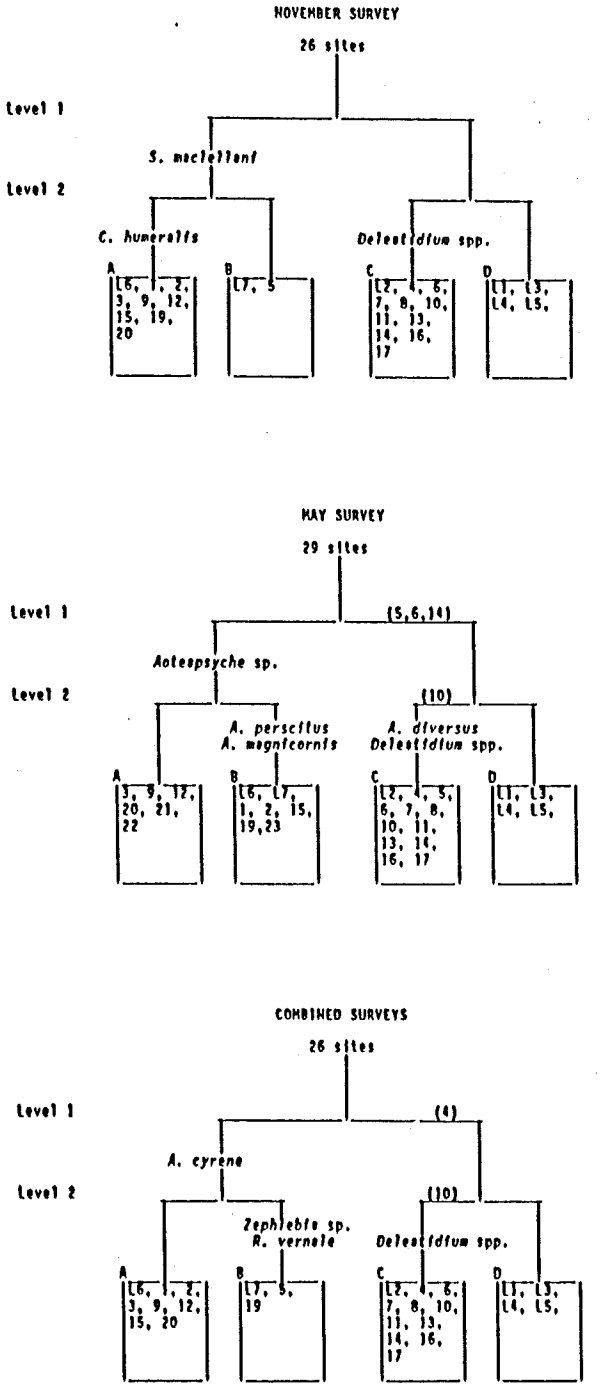


Figure 5.1. TWINSPAN classifications of 26-29 North Westland stream and river sites showing "indicator species". Presence/absence data were used to produce classifications from November 1986, May 1987 and combined surveys. Sites whose classification was borderline are shown in parentheses at the appropriate level.

TWINSPAN site groupings represented a gradient of physicochemical conditions with sites in Group A having the greatest pH, alkalinity and channel width, and the lowest DOC and total reactive Al concentrations (Table 5.3.). In contrast, Group D sites were small streams with very acid water containing high concentrations of DOC and Al. In addition, sites developed for pine forestry (i.e., most sites in Groups C and D) had higher summer water temperatures (mean > 22°C) than undisturbed sites (mean ~15°C).

TWINSPAN classified taxa into eight groups at level 3 (Table 5.2.). Taxa in Group I occurred exclusively in site Groups A and B. Groups II and III contained taxa found predominantly in site Groups A, B and C, whereas Groups IV, V, VI and VII were composed largely of "species" with little apparent site group preference. Group VIII contained taxa confined almost exclusively to site Groups C and D and included three primarily lentic species (*?Triplectidina* sp., *Rhantus pulverosus* and *Paradixa* sp.) which were found only in pools in streams draining recently modified catchments in LREA (Group D).

Table 5.3. Mean values (and 2 SE) for environmental variables and numbers of taxa in each TWINSPAN site group (both surveys combined). Physicochemical characteristics of all sites are given in Table 4.2. See Table 2.1. for rank order of development scores.

Variable	Group A	Group B	Group C	Group D
pH	6.1 (0.3)	5.0 (0.2)	4.6 (0.2)	4.4 (0.2)
Alkalinity ($g.m^{-3}CaCO_3$)	3.3 (1.0)	0.9 (0.4)	0.3 (0.2)	0.1 (0.3)
DOC ($g.m^{-3}$)	10.4 (3.2)	16.1 (5.8)	16.9 (4.2)	24.6 (7.8)
Conductivity ($mS.m^{-1}$)	2.8 (0.3)	2.4 (0.6)	2.7 (0.5)	3.8 (0.3)
Total reactive Al ($mg.m^{-3}$)	206 (65)	343 (8)	377 (79)	509 (169)
Streambed stability	37.3 (4.0)	27.3 (10.7)	30.7 (2.9)	46.3 (15.7)
Channel width (m)	5.2 (2.9)	4.0 (2.7)	2.5 (0.5)	1.3 (0.3)
Temperature (°C)	14.6 (1.9)	14.8 (0.3)	22.4 (2.3)	27.6 (2.2)
Rank order of development	1.0 (0.0)	1.0 (0.0)	3.3 (0.8)	4.3 (0.5)
Numbers of taxa	37.4 (2.6)	30.0 (9.5)	16.1 (2.1)	12.3 (3.3)

5.3.4. Ordination and Relationships with Environmental Variables

DECORANA axis 1 explained 59-64 % of the variation in the data sets, and 82-88 % was explained when axis 2 was included (Table 5.4.). When the first two DECORANA axes were plotted together, TWINSPAN site groupings separated out clearly with almost no overlap (Fig. 5.2.). Highly significant correlations were detected between DECORANA axis 1 and all environmental variables except conductivity and channel stability (Table 5.5.). Strongest correlations were with pH, alkalinity, temperature and rank order of development. In contrast, DECORANA axis 2 was not correlated strongly with any of the variables measured (Table 5.5.).

Principal component analysis (PCA) of the environmental variables generated three main factors which together explained 85 % of the variation in the data set (Table 5.6.). Factor one implicated the chemical nature of the water (pH, alkalinity, DOC and total Al) as the major component of the PCA. Because of strong intercorrelations between these variables (Table 4.3.), pH was selected to represent the water chemistry component in subsequent multiple regressions. Factors 2 and 3 of the PCA implicated channel stability, conductivity and temperature as other important variables, and they were used along with pH and channel width (also implicated by Factor 1) in multiple regression analyses. Following an initial series of regressions, channel stability, width and conductivity were discarded, and pH and temperature were retained as key variables. Their use yielded regression equations which had r^2 values between 0.79 and 0.92 (Table 5.7.).

5.3.5. Multiple Discriminant Analysis

Overall, MDA successfully allocated 88.5 % of the 26 sites to the correct site group on the basis of stream water pH and temperature. Best predictions (100 %) were for TWINSPAN Groups B and D whereas Group A and Group C sites were predicted with 87.5 and 81.8 % accuracy, respectively. Streamwater pH gave higher canonical coefficients than temperature for both MDA functions indicating that pH was more powerful at discriminating between sites (Table 5.8.).

Table 5.4. Eigenvalues and cumulative percentage variance of the data set explained by three DECORANA axes from each survey and both surveys combined.

Survey	Axis	Eigenvalue	Cumulative percentage variance explained
November	1	0.501	59.0
	2	0.210	83.7
	3	0.138	100.0
May	1	0.439	58.5
	2	0.179	82.3
	3	0.133	100.0
Combined	1	0.436	63.6
	2	0.169	88.3
	3	0.080	100.0

Table 5.5. Correlation coefficients (r_s for Rank, all others r) between DECORANA axes 1 and 2 (presence/absence data) and nine environmental variables measured in November 1986, May 1987 and combined surveys. Transformations were done on channel width, pH (both log(x)) and alkalinity (log(x+1)). Units are given in Table 5.3. *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$.

	November		May		Combined	
Variable	Axis 1	Axis 2	Axis 1	Axis 2	Axis 1	Axis 2
pH	-0.88***	-0.22	-0.84***	-0.26	-0.86***	-0.37
Alkalinity	-0.88***	-0.23	-0.84***	-0.27	-0.85***	-0.37
DOC	0.62***	0.25	0.66***	0.31	0.64***	0.41*
Conductivity	0.26	-0.10	0.39*	-0.04	0.35	0.10
Total reactive Al	0.75***	0.31	0.77***	0.24	0.74***	0.38
Streambed stability	0.05	-0.38	-0.01	0.00	0.05	-0.26
Channel width	-0.62***	-0.27	-0.67***	-0.35	-0.67***	-0.40*
Temperature	0.87***	-0.20	0.77***	-0.06	0.83***	-0.12
Rank order of development	0.85***	-0.14	0.74***	0.21	0.82***	-0.10

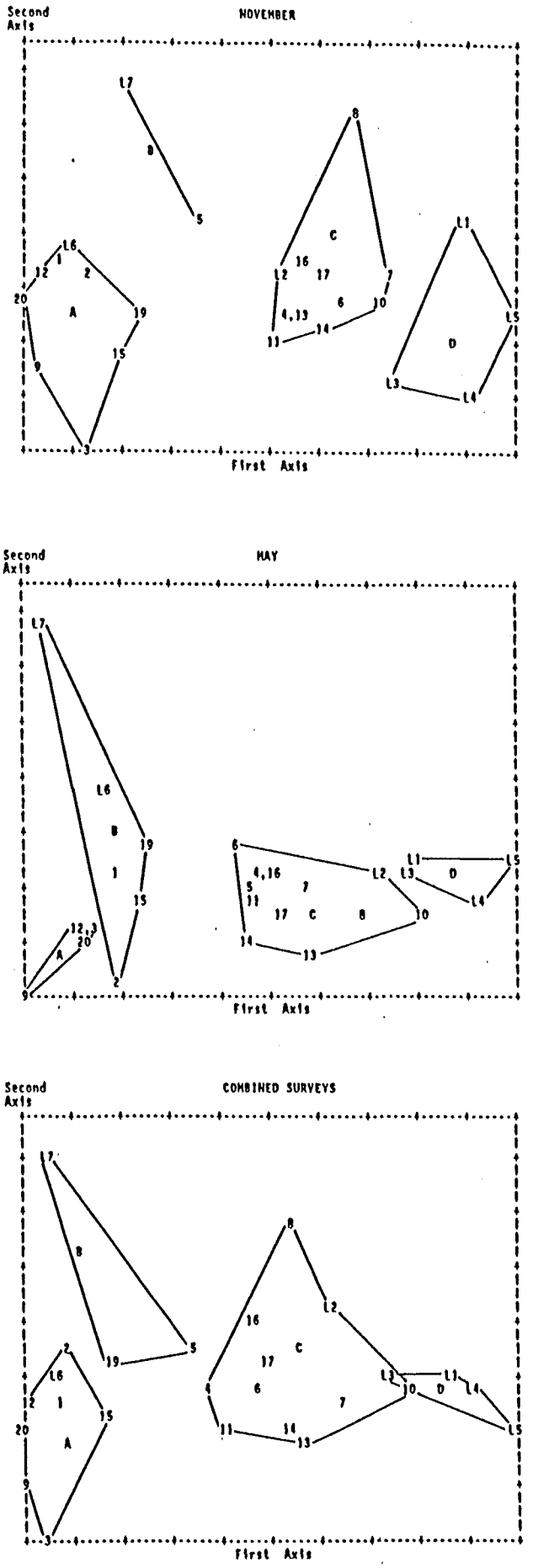


Figure 5.2. North Westland stream and river sites which were sampled twice plotted on DECORANA axes 1 and 2 using presence/absence data from November 1986, May 1987 and combined surveys. TWINSPAN site groupings at Level 2 (A-D) are also shown.

Table 5.6. Principal component analysis of eight environmental variables showing factor loading values for each variable, and eigenvalues and cumulative percentage variance of the data set explained by each factor. Units and details of transformations are given in Tables 5.3. and 5.5.

Variable	Factor 1	Factor 2	Factor 3
pH	0.447	-0.114	-0.144
Alkalinity	0.442	-0.159	-0.202
DOC	-0.410	-0.046	-0.366
Conductivity	-0.214	-0.476	-0.629
Total reactive Al	-0.402	0.212	-0.098
Streambed stability	0.050	-0.787	0.319
Channel width	0.342	0.203	-0.016
Temperature	-0.332	-0.166	0.545
Eigenvalue	4.39	1.34	1.08
Percentage variance explained	54.9	71.7	85.2

Table 5.7. Multiple regression equations (with r^2) derived using stream temperature (Temp) and log pH (PH) to describe DECORANA axis 1 from November, May and combined surveys (presence/absence data).

Survey	Regression equations	r^2
November	595.03 - 893.72PH + 9.25Temp	0.92
May	674.88 - 929.08PH + 6.49Temp	0.79
Combined	552.62 - 828.71PH + 7.54Temp	0.85

Table 5.8. Standardised coefficients for canonical variables of Functions 1 and 2 from a Multiple Discriminant Analysis of two key environmental variables using site groupings at TWINSPAN level 2 (both surveys combined). Coefficients indicate the relative contribution of each variable to the discrimination.

Variable	Function 1	Function 2
Log pH	33.55	20.75
Temperature	-0.22	0.25

5.4. DISCUSSION

Invertebrate faunas of North Westland streams

The many streams that drain the Larry River and Craigieburn terraces provide a wide range of physical and chemical habitats for invertebrates. Because of the proximity of streams and rivers in this region, intra-site differences in the taxonomic composition of benthic assemblages might be expected to reflect the ability of certain species to survive and maintain populations under the prevailing physicochemical conditions. Thus, based on species richness, forested streams on the Craigieburn pakihi provided the most favourable lotic habitat for invertebrate colonisation, and very acidic, developed, brownwater streams in LREA, the least favourable.

Chironomids, oligochaetes, and species of *Oxyethira* (Hydroptilidae), *Psilochorema* (Hydrobiosidae), *Hydora* (Elmidae) and *Deleatidium* (Leptophlebiidae) were found at most sites. The three last-named genera are amongst the most frequently occurring in West Coast streams in general (Winterbourn & Collier, 1987), and are considered to be moderately or very tolerant of changes in water quality (Winterbourn, 1981). However, only *Deleatidium* belongs to the "core element" of invertebrates which Rounick & Winterbourn (1982) identified in a wide variety of streams throughout New Zealand (chironomids were not considered in that study).

Many taxa (44) had sporadic distributions and were found at five or fewer sites where most were uncommon. Exceptions were *Megaleptoperla grandis*, a gripoterygid stonefly known to inhabit upland streams with stable beds (Winterbourn, 1981), the conoesucid caddis *Baraeoptera roria* which tends to have clumped distributions within a particular stream, and *Olinga feredayi* and *Pycnocentria evecta* (both conoesucids) which are widely distributed in other parts of New Zealand and often common (Cowley, 1978; Winterbourn & Gregson, 1981). With the exception of *O. feredayi*, these taxa were collected from cool, forested North Westland streams with pH in the range 4.8 to 6.6. *O. feredayi* was not found in North Westland streams with pH < 5.2 and Winterbourn & Collier (1987) did not record it at < 5.5.

In contrast to findings in some Northern Hemisphere acid streams (e.g., Sutcliffe & Carrick, 1973; Simpson *et al.*, 1985), faunas in acid, brownwater streams in North Westland were not characterised by the absence of Ephemeroptera and the predominance of Plecoptera. Indeed, the mayflies *Deleatidium* spp., *Ameletopsis perscitus* and *Zephlebia* sp. tolerated a wide range of physicochemical conditions, although *Coloburiscus humeralis* and

Nesameletus sp. had more restricted distributions and were found only in cool streams with pH down to 4.6 and 5.4, respectively. Winterbourn & Collier (1987) did not record the latter taxon in undisturbed streams with pH < 5.0. *Spaniocercoides cowleyi* was the most widespread stonefly in the North Westland streams, occurring even in the very acidic and relatively warm waters of Sites L1, L3, L4 and L5 on the Larry River pakihi. Nine of the 15 stonefly taxa recorded were found only at sites in TWINSPAN Groups A and B (mean pH ≥ 5.0), but several of them were collected by Winterbourn & Collier (1987) from more acidic waters. Species of *Helicopsyche*, *Aoteapsyche* and *Hydrobiosella* (all Trichoptera) were not collected in streams with pH < 5.0 in that survey, but were found in some North Westland streams with pH as low as 4.6-4.8. Of the taxa found predominantly at disturbed sites, several (e.g., *Sigara* sp., *Liodessus plicatus* and *Rhantus pulverosus*) come to the water surface to take in air and are frequently common in ponds and backwaters (Winterbourn & Gregson, 1981). Larvae of the *?Triplectidina* species also are usually found in small, lentic habitats and are one of the few insects present in mountain tarns (Cowley, 1978).

Factors affecting invertebrate distributions

The pH and temperature of stream water appeared to be major factors affecting the composition of benthic invertebrate assemblages in the North Westland streams considered in this study. In contrast, Winterbourn & Collier (1987) found no relationship between taxonomic richness of the benthos and pH in an earlier survey of Westland streams, but most sites included in that survey drained native forested catchments and had pH > 4.5.

TWINSPAN initially separated benthic communities in very acidic streams (pH almost always < 5.0 and as low as 4.1) surrounded by induced pakihi or pine forest (disturbed), from less acidic (pH > 4.5) streams flowing mainly through native forest (undisturbed). On average, streams with relatively high summer water temperatures (related to degree of catchment development), and/or very acidic, brown waters supported almost half as many taxa as cool, less acidic streams in the same region. The subsequent separation of disturbed sites may have as its basis differences in water temperature which were higher in summer at the most recently developed (Group D) sites.

Effects of catchment development

Impacts of forestry practices on stream ecosystems include the alteration of flow and thermal regimes, increases in light levels, reductions in allochthonous inputs, changes in nutrient inputs and greater sedimentation (Morgan & Graynoth, 1978; Ward, 1984; Winterbourn, 1986). Responses of stream invertebrates to these changes vary, and densities of some taxa increase whereas others decline (e.g., Graynoth, 1979; Newbold *et al.*, 1980; Wallace & Gurtz, 1986). The presence of higher densities of some species in streams draining clear-cut catchments is often ascribed to greater microbial conditioning and hence improved nutritive quality of detritus, and higher periphyton biomass because of more light, warmer temperatures and increased nutrient inputs (Hawkins *et al.*, 1982). In some cases, these changes may offset potentially detrimental effects of high sedimentation (e.g., Murphy *et al.*, 1981). Conversely, warmer water temperatures and greater microbial activity can reduce dissolved oxygen concentrations to levels which may be lethal to some invertebrates (Morgan & Graynoth, 1978).

With the exception of Site L2 which drains induced pakihi covered with manuka forest, disturbed sites in North Westland (TWINSPAN site Groups C & D) all had summer temperatures greater than 19°C, and averages were up to 13°C higher than at undisturbed sites. Brown & Krygier (1970) reported maximum increases in water temperature of 15.5°C in Oregon streams one year after clear-cutting. Temperature tolerances of aquatic insects vary, with some species of Plecoptera and Trichoptera dying at about 20°C, although sublethal effects of temperature on metabolism, growth and emergence (Wiederholm, 1984) may be more important in limiting distributions. In North Westland streams with summer temperatures above 25°C (Group D), an average of 12 taxa were taken, whereas an average of 16 were collected from streams where summer temperatures averaged 22°C. High summer water temperatures (or associated factor(s)) therefore may have limited the distributions of some invertebrate species in North Westland streams. Faunas of Group D streams were distinguished from those of other disturbed sites by the absence of *Deleatidium* which was found in nearby Site L2.

Other factors such as increased sedimentation and changes in the discharge regime also could have affected benthic faunas in developed streams. Jackson (1987) showed that, in the year after development of catchment L3 in LREA, sediment transport was an order of magnitude higher and major floods (> 10 $l.s^{-1}.ha^{-1}$) three times more frequent than for

the control catchment (L2). However, sediment yields normally return to predisturbance levels within two years of v-blading (R.J. Jackson, pers. comm.) and, because of frequent floods, sediment does not accumulate over long periods in these streams. Thus, direct effects of sedimentation on aquatic life should not be pernicious in streams draining catchments developed more than two years before my survey was conducted, and are unlikely to account for the depauperate faunas at Sites 4, 10, 11, 13, 14, L1, L4 and L5.

Interestingly, Site 16 which is surrounded by native forest with no evidence of upstream development had a summer water temperature of 22°C and pH < 4.5, and was grouped with developed sites in TWINSPAN Group C. This suggests that streamwater physicochemistry can be more important than other development-related factors such as sedimentation in determining benthic invertebrate community composition in these North Westland streams.

In summary, one effect of v-blading appears to have been to increase summer water temperatures at some sites to levels which may be detrimental to stream invertebrates, particularly in streams draining developed catchments on the Larry River pakihi. However, benthic faunas appeared to recover from the initial impacts of forestry development within a relatively short time and distance, although apparent recovery may also have been linked to an increase in water pH. Thus, Sites 3, 21 and 22 all occurred in the lower reaches of rivers draining some developed catchments and were classified with undisturbed sites in TWINSPAN Group A, and Sites 5 and L7, which were surrounded by native forest but were a few hundred metres downstream of catchments v-bladed in 1985-86, had faunas that were similar, overall, to those of undisturbed Site 19. Because faunas in undeveloped streams flowing from induced pakihi (e.g., Site L2) were at least as depauperate as those in streams draining developed catchments, it is apparent that conditions other than temperature also affect species richness at the head waters of pakihi streams.

Effects of pH

High acidity is believed to affect aquatic invertebrates directly by disrupting ionic regulation and calcium metabolism, and by the mobilisation of toxic metals such as Al into the water column (Haines, 1981). In Chapter 4, I showed that concentrations of labile monomeric Al were low in Westland streams compared with many acid clearwater streams in the Northern Hemisphere. Thus, Al toxicity is unlikely to be a problem for invertebrates colonising brownwater streams in New Zealand, although acute

levels have yet to be established for any taxa. Preliminary work by Havas & Likens (1985) suggested that Al (mostly hydroxide complexes) may not become toxic to some species of Crustacea and Chironomidae until concentrations approach or exceed 1000 $mg.m^{-3}$, and Havas (1985) even reported that Al (1020 $mg.m^{-3}$ at pH 4.5) temporarily ameliorated hydrogen ion toxicity to *Daphnia magna* which normally is very sensitive to low pH.

Estimates of lethal pH levels for aquatic invertebrates vary depending on the species and life history stage. In general, caddisflies appear to be more tolerant of low pH than mayflies, and emergence is frequently the most sensitive period (Bell & Nebeker, 1969; Bell, 1971). Bell (1970) showed that the midge *Tanytarsus dissimilis* was unable to complete its life cycle at pH < 5.5 whereas Burton & Allan (1986) found that survival of one snail, two caddisfly and one stonefly species collected from circumneutral streams in Michigan decreased significantly at pH 4 but not pH 5. In contrast, van Frankenhuyzen *et al.* (1985) showed that eggs of the caddis *Clistoronia magnifica* developed normally at pH 4 and that larvae grew faster at pH 4.2-5.2 than at pH 5.8-6.4.

In the present study, streams with the most impoverished benthic faunas not only had the warmest temperatures but also the lowest pHs (usually < 5.0), whereas undisturbed sites all had pH > 4.5 and were colonised by relatively large numbers of species. If pH was a major factor affecting benthic invertebrate faunas at undisturbed sites with pH > 4.5, then indicator species would be expected to be present only in the less acidic streams (i.e., Group A). This obviously was not the case (i.e., almost all indicator species were for Group B not Group A), and indicates that most of the stream invertebrate taxa found in North Westland can survive down to a lower limit of about pH 4.5. This confirms the findings of Winterbourn & Collier (1987) and shows that their conclusions were not affected by geographic factors. Thus, most streams flowing out of pakihi bogs appear to be too acidic in their head waters to support a diverse invertebrate fauna, but when pH increases above 4.5, acidity does not seem to be a factor limiting population maintenance in streams.

CHAPTER 6

DYNAMICS OF BENTHIC INVERTEBRATES IN

SOUTH WESTLAND STREAMS

6.1. INTRODUCTION

Invertebrate faunas of Northern Hemisphere acid streams often have fewer species, lower densities and different taxonomic and functional compositions than nearby sites where the pH of water is higher (e.g., Hall *et al.*, 1980; Townsend *et al.*, 1983; Mackay & Kersey, 1985; Simpson *et al.*, 1985). Herricks & Cairns (1974) recorded a fall in benthic invertebrate densities of almost 50 % when an alkaline stream (pH 8.0) in Virginia was acidified experimentally to pH 4.0 for 15 minutes, and Kimmel *et al.* (1985) found that numbers of invertebrates in a circumneutral (pH 6.1-7.4) Pennsylvanian stream were about 2.5-11.0 times higher than in a nearby stream with pH 4.6-6.0. The latter authors collected several taxa of mayflies (mostly *Baetis* and *Ephemerella* spp.) in all seasons from the circumneutral site but found them rarely in the more acidic stream.

In streams draining Hubbard Brook catchments, densities of *Ephemerella funeralis* were found to increase as pH increased even though experimental acidification showed that this species could tolerate pH 4 for up to three months (Fiance, 1978). However, larvae of *E. funeralis* at the acidified site were 29 % smaller than their counterparts at the reference site, and Fiance (1978) interpreted this to mean that more energy was being allocated to maintain internal ionic balance under acidic conditions. Although Fiance (1978) discounted decreased quantity or quality of food as a reason for reduced growth of *E. funeralis* at low pH, several other workers have implicated food as a major factor influencing invertebrate community dynamics in acid streams (e.g., Sutcliffe & Carrick, 1973; Otto & Svensson, 1983; Townsend *et al.*, 1983). The two latter groups of authors both found fewer species of grazers in acid streams, but representation of other feeding groups was inconsistent.

Findings presented in Chapter 5 and by Winterbourn & Collier (1987) indicate that acidity is not a primary factor affecting invertebrate species richness in Westland streams with pH above about 4.5. However, low pH could have sublethal effects on some benthic taxa, either physiologically or by reducing their food supply. If so, it might be predicted that densities, biomass and production of sensitive invertebrate species would be lower than in otherwise comparable streams of circumneutral pH. To investigate this possibility, I collected quantitative benthic samples bimonthly over a 12 month period from two acid, brownwater streams (Steep Creek and Suspect Stream) and two circumneutral, clearwater streams (Hidden Creek and Toilet Stream)

in South Westland (see Fig. 2.3.). As shown in Chapter 4, these two pairs of undisturbed sites have distinct chemical "signatures" with pH in the range 4.3 to 5.7 at the brownwater sites, and 6.6 to 8.0 at the clearwater sites. In addition to investigating densities of benthic communities as a whole, I studied population dynamics (size, sex ratios, biomass, life histories and production) of *Deleatidium* spp. (Ephemeroptera) because of the apparent sensitivity of mayflies to low pH, and because this taxon is present in most Westland streams (see Chapter 5 and Winterbourn & Collier, 1987). Gut contents of selected taxa from the four sites were examined to determine whether differences in diet might be a factor influencing their success in one or other of these environments (brownwater or clearwater).

6.2. METHODS

6.2.1. Benthic Invertebrate Sampling

Benthic macroinvertebrates were collected bimonthly between March 1985 and February 1986 from stony, riffle areas in Hidden Creek, Toilet Stream, Steep Creek and Suspect Stream. Sites were sampled with a 0.5 mm mesh Surber sampler by agitating the benthos and brushing stones within the 0.1 m^2 quadrat. Five replicate samples were taken on each occasion from the same reach of each stream except that four samples were taken from Steep Creek in March and Toilet Stream in May. All benthic samples were preserved with 70 % ethanol in the field and were sorted and identified under a binocular microscope. Identifications of invertebrates were made as described in Section 5.2.1.; ostracods were not separated below class.

6.2.2. Analysis of *Deleatidium* Populations

Biomass

Bimonthly collections of *Deleatidium* larvae from the four South Westland streams were dried (50°C for 5 days) and weighed (0.1 mg) to determine total biomass. Because samples were kept in 70 % ethanol for varying periods, some loss of organic weight may have occurred, although larvae probably achieved a fairly constant weight after about 30 days (Howmiller, 1972). By this time, *Deleatidium* larvae can lose on average 26.7 % of initial dry weight (Winterbourn, 1974), and biomass values were corrected accordingly.

Measurements of larvae

All measurements were made with a Wild Heerbrug stereomicroscope fitted with an electronic micro-length measuring attachment. This device measures accurately to 0.01 mm and was calibrated before use with a stage micrometer. Head width across the eyes of all final instar *Deleatidium* larvae (distinguished by fully developed wing pads) was measured to determine if significant differences in maximum larval sizes occurred between sexes and sites.

Size-frequency distributions were constructed from head width measurements of up to 278 larvae per bimonthly collection from the four

streams. Older larvae (head widths ≥ 1.00 mm) were sexed by eye dimorphism; males can be distinguished from females by a double pair of eyes. When collections were very large, the whole sample was stirred in a petri dish marked into quarters and only larvae settling in one or two randomly selected quadrants were measured. Animals with bodies (excluding cerci) touching the dividing lines were included in the subsample. Validation of this subsampling procedure was obtained by comparing sizes of larvae from one quadrant with those from a whole sample. The subsample size-frequency distribution deviated from the true distribution by < 2 % for any size class.

Production estimates

Annual production of *Deleatidium* at the four sites was calculated using the Size-frequency (Hynes) method (Hamilton, 1969; Benke, 1979) which assumes that an average size-frequency distribution obtained from samples taken over a year will approximate the mean survivorship of a hypothetical "average cohort" (Benke, 1984). The method does not require that discrete cohorts be identified, an important advantage when calculating production of taxa like *Deleatidium* spp. which can have poorly-synchronised life histories (Winterbourn, 1974; Towns, 1981; Towns, 1983b).

Production of *Deleatidium* at each site was estimated from six bimonthly samples. Mean annual densities (number per m^2) were calculated for nine size classes (0.20-2.00 mm head width), and converted to biomass using a dry weight to head width relationship provided by M.J. Winterbourn. Weight losses between successive size classes were summed and multiplied by the number of size classes to provide an estimate of production (Benke, 1984). Apparent negative production, which occurred only in the first two size classes (0.20-0.60 mm head width), was not included in the final summation, as recommended by Benke & Wallace (1980). All populations were treated as univoltine (i.e., cohort production index = 1; see Section 6.3.2.).

6.2.3. Gut Content Analyses

Collection of invertebrates

Benthic kick samples (1 mm mesh net) were taken from Hidden Creek, Toilet Stream, Steep Creek and Suspect Stream in November 1986 and May 1987, and were preserved with 10 % formalin in the field. Four insect taxa were sorted from the samples for gut content analyses: *Deleatidium* spp., *Austroperla cyrene*, *Stenoperla maclellani* and *Zelandobius confusus*. These

taxa were known to occur in all four streams, but larvae of *Z. confusus* were more abundant at the brownwater sites whereas the other taxa were more common at the clearwater sites (see Table 6.2.).

Preparation of gut contents

Gut contents of the selected taxa were prepared for examination as described by Cowie (1980). Head widths of larvae were measured with a calibrated eyepiece graticule and guts were excised from up to ten similar-sized larvae from each site (Table 6.1.). No larvae of *A. cyrene* were collected in May and no *Z. confusus* were taken in November from Suspect Stream.

Contents of midguts and/or foreguts (depending on degree of fullness) were teased into a watchglass containing distilled water and, after transfer to a test tube, were dispersed for 45-60 seconds with a Mettler Electronic ultrasonic cleaner. The dispersed material was filtered on to a membrane filter (0.45 μm) through a Millipore funnel (16 mm diameter) fitted when appropriate with tapered, perspex shims (8 or 5 mm inner diameter) to concentrate material. Filters containing gut contents were mounted on slides in lactophenol-PVA stained with Lignin Pink and dried at 37^{o}C for five weeks before examination.

Examination of gut contents

Filters mounted on slides were viewed at 400 times magnification with a Wild Heerbrug M20 phase-contrast microscope fitted with a gridded eyepiece. Food items were classified into one of eight categories (see legend to Fig. 6.7.). The "other" category included all material which was not readily placed in any other group and always comprised less than 4 % of total gut contents. On each slide, 20-30 randomly selected fields were viewed and items cut by ten cross hairs on a transect through each field were recorded.

Table 6.1. Range of body lengths (*A. cyrene* only) or head widths (all other taxa) (mm) of larvae used for gut content analyses, and number of guts pooled for each analysis (parentheses). N, November 1986; M, May 1987. -, no guts examined or guts empty.

		Hidden Creek	Toilet Stream	Steep Creek	Suspect Stream
Deleatidium spp.	N	1.3-1.5 (10)	1.3-1.5 (10)	1.3-1.5 (10)	1.3-1.5 (10)
	M	1.2-1.5 (10)	1.2-1.5 (10)	1.3-1.5 (10)	1.3-1.5 (10)
Zelandobius confusus	N	-	-	0.9-1.3 (10)	-
	M	-	-	0.8-1.1 (10)	0.9-1.0 (10)
Stenoperla maclellani	N	1.8 (1)	2.0-2.3 (5)	2.2-2.5 (2)	1.7-1.9 (2)
	M	1.8-2.4 (3)	-	1.6-2.5 (5)	1.9 (1)
Austroperla cyrene	N	8.2-10.2 (4)	9.0-11.0 (4)	8.5-11.2 (4)	11.5 (1)
	M	8.8-9.8 (4)	7.9-11.2 (4)	4.8-7.0 (2)	-

6.3. RESULTS

6.3.1. Composition and Density of Invertebrate Faunas

Taxonomic richness

Overall, 74 taxa were collected from the four South Westland streams during the study, and over 80% of these were insects (Table 6.2.). Almost all insect orders were better represented at the clearwater sites where 64 invertebrate taxa were recorded during the study, 56 in Toilet Stream (Table 6.3.). By comparison, 47 taxa were collected from the two brownwater streams which contained fewer representatives of all insect orders except Megaloptera. Nevertheless, only six more taxa were recorded in Hidden Creek (clear) than Steep Creek (brown) where all insect orders were represented by very similar numbers of taxa (Table 6.3.). The total number of taxa collected on each sampling occasion was relatively constant at the four sites (Fig. 6.1.), although not all were taken at any one time. Numbers were consistently higher in the clearwater streams (30-38 taxa) whereas Suspect Stream always had the lowest number of taxa (19-24).

Sixteen of the taxa (including the *myzobranchia* subgroup of *Deleatidium*; see later) common to both clearwater streams were not found at either acid site (Table 6.2.). Six of these taxa were Trichoptera, although only *Philorheithrus agilis* larvae were abundant at any site (mean > 50 m^{-2}). *Nesameletus* sp. (Ephemeroptera) was also common in both clearwater streams but was not found at the brownwater sites where another mayfly, *Ameletopsis perscitus*, was relatively abundant. The latter was one of only five taxa which were taken exclusively from both brownwater streams (Table 6.2.).

Invertebrate densities

Bimonthly densities of benthic invertebrates at the four South Westland sites ranged from 580 to 8436 individuals m^{-2} and, except in January, were always highest at the two clearwater sites (Fig. 6.2.). Large numbers of chironomid larvae were responsible for the high total invertebrate density in Steep Creek in January (see Fig. 6.3.). The number of species taken was temporally most variable in Toilet Stream and Steep Creek (CV = 47 % and 45 %, respectively) followed by Suspect Stream (CV = 36 %) and Hidden Creek (CV = 26 %). Comparable temporal patterns of abundance were found at the clearwater sites. Distinct peaks occurred in July when sampling was preceded by a prolonged dry spell, and troughs were observed in September

TRICHOPTERA				
Helicopsyche sp.	+	13	0	0
Rakiura vernale	0	0	23	0
Oeconesus sp.	43	15	0	0
Philorheithrus agilis	137	65	0	0
Olinga feredayi	484	75	0	+
Conuxia gunni	+	0	+	0
Triplectides sp.	0	+	+	0
Zelolessica cheira	+	0	112	16
Alloecentrella magnicornis	0	0	10	+
Aoteapsyche sp.	0	+	0	0
Oxyethira albiceps	0	+	21	+
Paroxyethira (*eatoni* complex)	+	0	+	+
Ecnomidae	0	+	+	0
Hydrobiosella sp.	25	14	+	+
Polyplectropus sp.	0	+	+	+
Costachorema sp.	11	+	0	0
Hydrobiosis sp.	12	+	+	0
Edpercivalia maxima	+	+	0	0
Hydrochorema tenuicaudatum	+	+	0	0
Hydrochorema crassicaudatum	+	0	0	0
Psilochorema sp.	0	+	11	12
MEGALOPTERA				
Archichauliodes diversus	0	0	19	12
COLEOPTERA				
Podaena sp.	+	+	+	+
Helodidae	0	+	+	14
Hydophilidae	0	+	+	0
Hydora sp.	56	41	158	26
Ptilodactylidae	+	+	0	0
DIPTERA				
Chironomidae	882	502	613	152
Austrosimulium sp.	33	35	+	+
Ceratopogonidae	+	+	26	19
Empididae	44	12	17	+
Psychodidae	+	+	+	0
Stratiomyidae	0	+	0	0
Neocurupira hudsoni	0	+	0	0
Hexatomini sp.A	29	15	+	+
Hexatomini sp.B	+	+	+	0
Eriopterini	18	30	+	0
Aphrophila neozelandica	+	0	0	0
Paralimnophila skusei	0	+	0	0
Zelandotipula sp.	0	0	0	+
Limonia sp.	+	+	0	0
Muscidae	+	+	+	+

*, Two subgroups (*lillii* and *myzobranchia*) were present in Hidden Creek and Toilet Stream, whereas only the *lillii* subgroup was found at the brownwater sites.

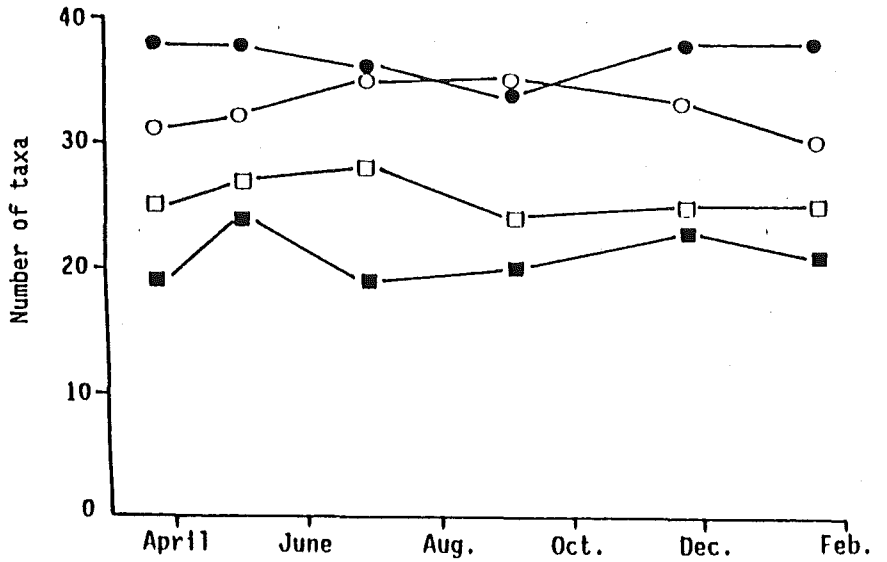


Figure 6.1. Numbers of benthic invertebrate taxa recorded in Hidden Creek (○), Toilet Stream (●), Steep Creek (□) and Suspect Stream (■) on six dates in 1985-86.

Table 6.3. Numbers of insect and total invertebrate taxa taken from clearwater and brownwater streams between March 1985 and February 1986.

	Clearwater			Brownwater		
Sites	Hidden	Toilet	Total	Steep	Suspect	Total
Ephemeroptera	4	5	5	2	2	2
Plecoptera	7	10	11	7	7	10
Trichoptera	13	15	19	12	8	13
Diptera	11	13	14	9	7	10
Coleoptera	3	5	5	4	3	4
Megaloptera	0	0	0	1	1	1
Total invertebrates	47	56	64	41	33	47

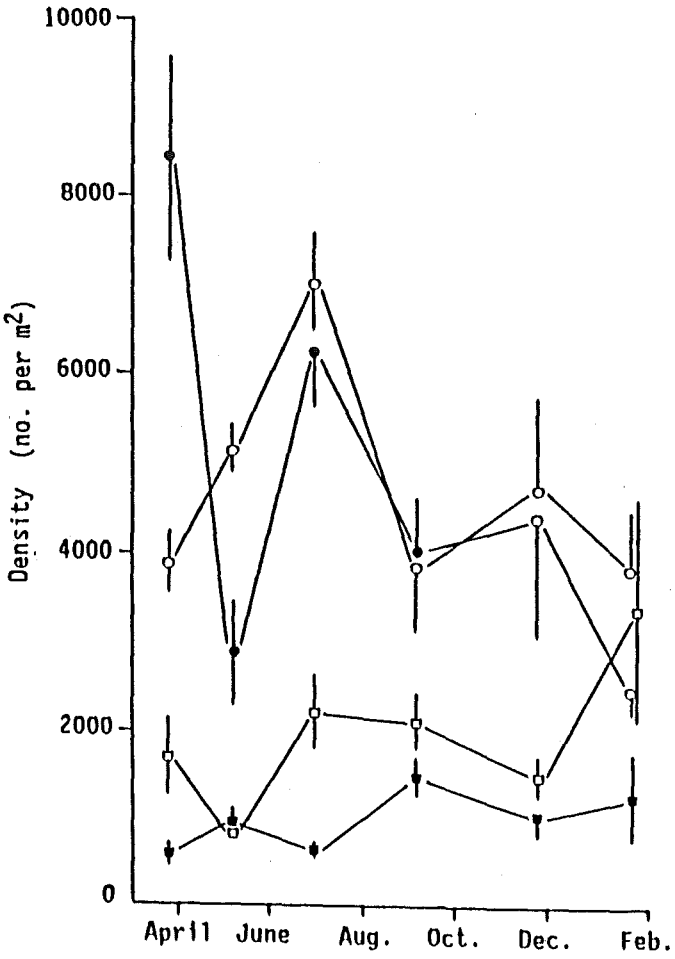


Figure 6.2. Densities ($\bar{x} \pm 1$ SE, n = 4-5) of benthic invertebrates collected from Hidden Creek (○), Toilet Stream (●), Steep Creek (□) and Suspect Stream (■) on six dates in 1985-86. Error bars are not shown if accomodated within the symbol.

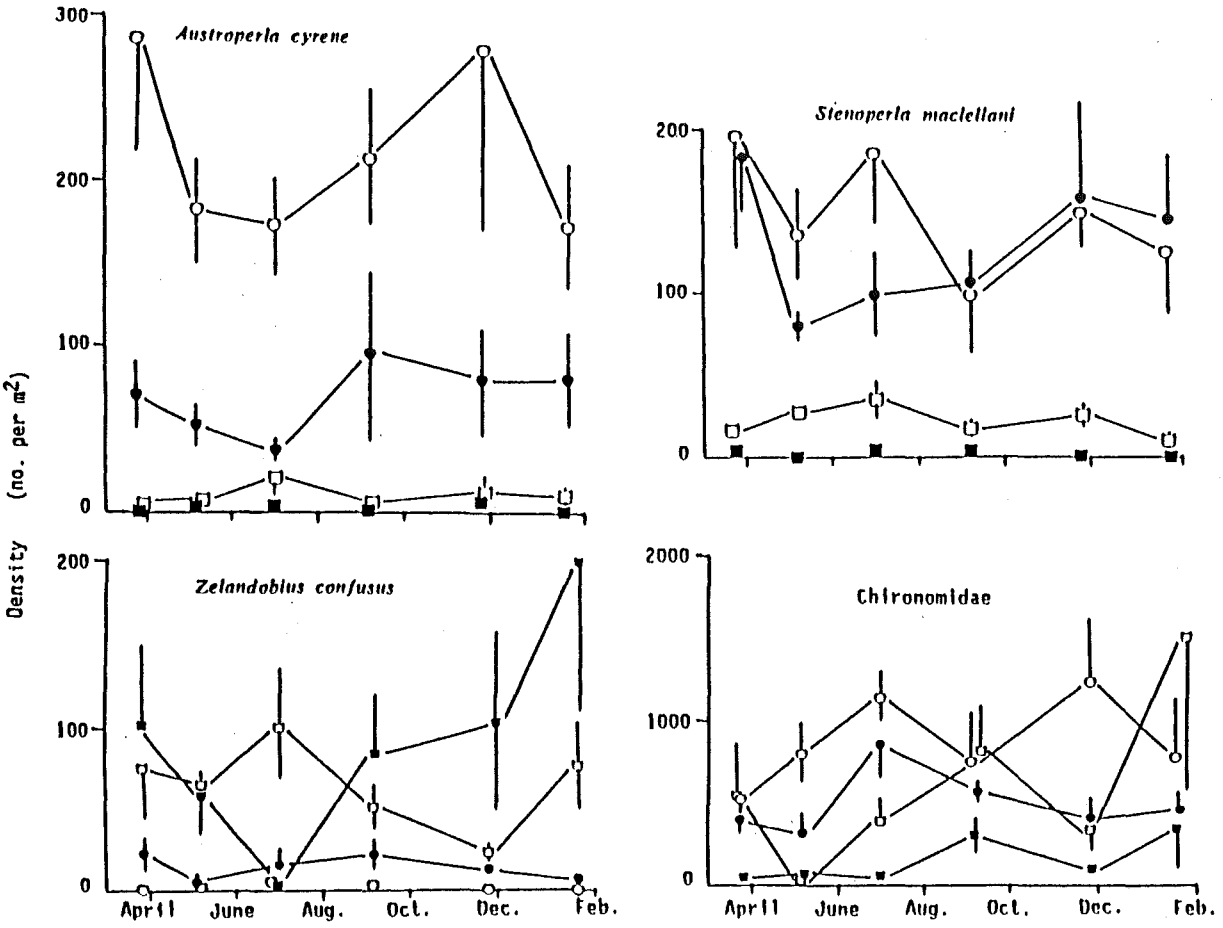


Figure 6.3. Densities ($\bar{x} \pm 1$ SE, n = 4-5) of larval *Austroperla cyrene*, *Stenoperla maclellani*, *Zelandobius confusus* (all Plecoptera) and Chironomidae collected from Hidden Creek (○), Toilet Stream (●), Steep Creek (□) and Suspect Stream (■) on six dates in 1985-86. Error bars are not shown if accomodated within the symbol.

when flows were relatively high (see Table 4.7.). Benthic invertebrate densities at the brownwater sites did not show the same temporal pattern even though they had similar flow regimes.

Deleatidium spp. larvae (Ephemeroptera) were the most common benthic invertebrates at all sites except Toilet Stream where the hydrobiid snail, *Potamopyrgus antipodarum*, was most abundant (Table 6.2.). At the clearwater sites, *Deleatidium* populations included species belonging to the informal *myzobranchia* and *lillii* subgroups (Winterbourn & Gregson, 1981), whereas only the *lillii* subgroup was found in the brownwater streams (see Section 6.3.2. for further results). Chironomid larvae were also common at all sites, with mean annual densities between 152 and 882 m^{-2} (Table 6.2.). Densities of chironomids fluctuated considerably at both brownwater sites (CV = 93 % and 85 % in Suspect Stream and Steep Creek, respectively), but their numbers were relatively constant in Toilet Stream (CV = 39 %) and Hidden Creek (CV = 30 %) (see Fig 6.3.).

Other taxa which were present at all sites and were abundant (average > 50 individuals m^{-2} in one or more streams) were the elmid beetle *Hydora* sp. which was most common in Steep Creek, ostracods, oligochaetes, and the stoneflies *A. cyrene* and *S. maclellani* (Table 6.2.; see also Fig. 6.3.). Mean annual densities of the three last-named taxa were 3-22 times higher in the clearwater streams than at either brownwater site. In contrast, mean annual densities of another stonefly, *Z. confusus*, were almost always much greater in the brownwater streams and were highest in Suspect Stream (Table 6.2; see also Fig. 6.3.).

6.3.2. *Deleatidium* Populations

Densities and biomass

Both density and biomass of *Deleatidium* were highest in Hidden Creek (1416-2318 m^{-2} and 0.112-0.376 g dry weight.m^{-2}, respectively) on all sampling dates except in March when densities were highest in Toilet Stream (Fig. 6.4.). The latter site almost always had more larvae than Steep Creek or Suspect Stream where densities were similar on most dates (range 234-1054 m^{-2}). In May, Toilet Stream had the lowest *Deleatidium* biomass recorded during the study (0.020 g.m^{-2}), but at other times biomass was similar to that in Steep Creek and Suspect Stream. Densities were most variable in Toilet Stream (CV = 52 %) followed by Suspect Stream, Steep Creek and Hidden Creek (CV = 45 %, 44 % and 20 %, respectively).

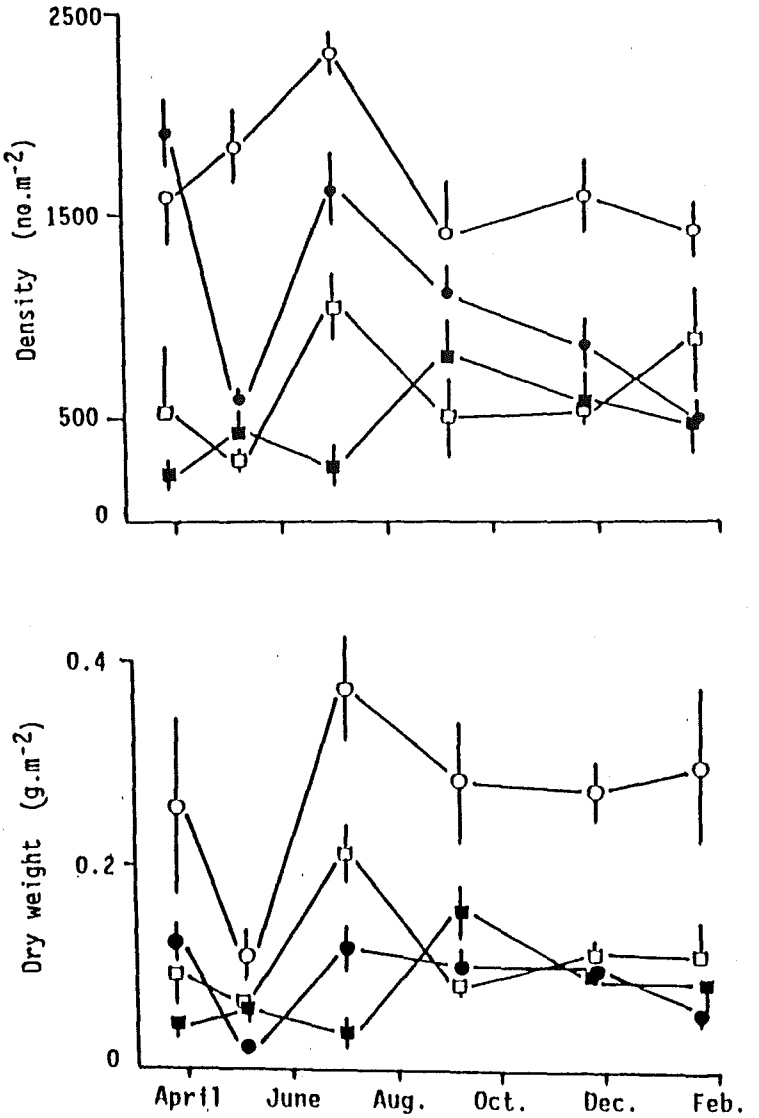


Figure 6.4. Densities and dry weights ($\bar{x} \pm 1$ SE, n = 4-5) of *Deleatidium* (Ephemeroptera) larvae collected from Hidden Creek (○) Toilet Stream (●), Steep Creek (□) and Suspect Stream (■) on six dates in 1985-86. Error bars are not shown if accomodated within the symbol.

Final instar sizes and larval sex ratios

Final instar male and female larvae could not be distinguished on the basis of size at any site (Table 6.4.), and neither could final instar larvae of the *lillii* and *myzobranchia* subgroups in Hidden Creek (Mann-Whitney U, $P > 0.05$). However, significant differences in maximum larval size (both sexes and subgroups combined) were apparent between sites (Kruskal-Wallis test, $P < 0.001$) with largest mean final instar larval size recorded in Hidden Creek, and the smallest in Suspect Stream. Similar proportions of female and male *Deleatidium* larvae with head widths $\geq$ 1.00 mm were found in Hidden Creek, Steep Creek and Suspect Stream (52-56 % females and 44-48 % males), but in Toilet Stream females were much more abundant (64 %).

Table 6.4. Head widths (mm) of final instar *Deleatidium* larvae (male, female and combined sexes) collected from four South Westland sites between March 1985 and February 1986.

	Mean	S.D.	n	Range
Hidden				
male	1.71	0.09	31	1.55-1.95
female	1.72	0.11	15	1.50-1.95
combined	1.71	0.09	46	1.50-1.95
Toilet				
male	1.74	0.07	2	1.69-1.79
female	1.66	0.07	3	1.58-1.72
combined	1.69	0.08	5	1.58-1.79
Steep				
male	1.64	0.07	8	1.54-1.72
female	1.67	0.13	16	1.50-1.92
combined	1.66	0.11	24	1.50-1.92
Suspect				
male	1.60	0.09	17	1.45-1.76
female	1.57	0.17	10	1.39-2.00
combined	1.59	0.12	27	1.39-2.00

Size-frequency distributions

The life history patterns of *Deleatidium* were indistinct at all sites and most size groups of larvae were present on all dates in all streams (Fig. 6.5.). *Deleatidium* populations were dominated by small individuals on most dates, although few larvae with head widths less than 0.4 mm were collected, presumably because most passed through the 0.5 mm mesh net. The preponderance of small larvae was most apparent in Toilet Stream where 87 % of all larvae collected had head widths < 1.00 mm. Larvae with head widths < 1.00 mm made up 74 % and 78 % of individuals in the brownwater streams, and 69 % in Hidden Creek. Final instar larvae were present in all bimonthly samples obtained from Hidden Creek, Steep Creek and Suspect Stream except those taken in July (Fig. 6.6.), and were most abundant in summer (November, January or March). In Toilet Stream, only five final instar larvae were collected during the study period and they were taken in November and January.

Production estimates

Although size-frequency distributions did not reveal clear life history patterns, the predominance of final instar larvae in summer suggested that there was probably one generation per year at all sites. Thus, a cohort production index of one was assumed when calculating annual production. *Deleatidium* production at the four sites ranged from 2.49 to 10.35 g dry weight.$m^{-2}.y^{-1}$ and annual biomass was between 0.38 and 1.57 $g.m^{-2}$ (Table 6.5.). Both production and biomass were highest in Hidden Creek and lowest in Suspect Stream. Annual production/biomass ratios (Table 6.5.) are believed to be related to individual growth rates and are roughly equivalent to biomass turnover rates (Benke, 1984). P/B ratios were similar at all sites and ranged from 6.2 (Steep Creek) to 7.2 (Toilet Stream).

Table 6.5. Annual production (P), biomass (B) and P/B ratios for *Deleatidium* populations at four South Westland streams between March 1985 and February 1986. All values are dry weights.

	Clearwater		Brownwater	
	Hidden	Toilet	Steep	Suspect
Production $g.m^{-2}.y^{-1}$	10.35	3.77	3.68	2.49
Biomass $g.m^{-2}$	1.57	0.53	0.59	0.38
P/B y^{-1}	6.6	7.2	6.2	6.6

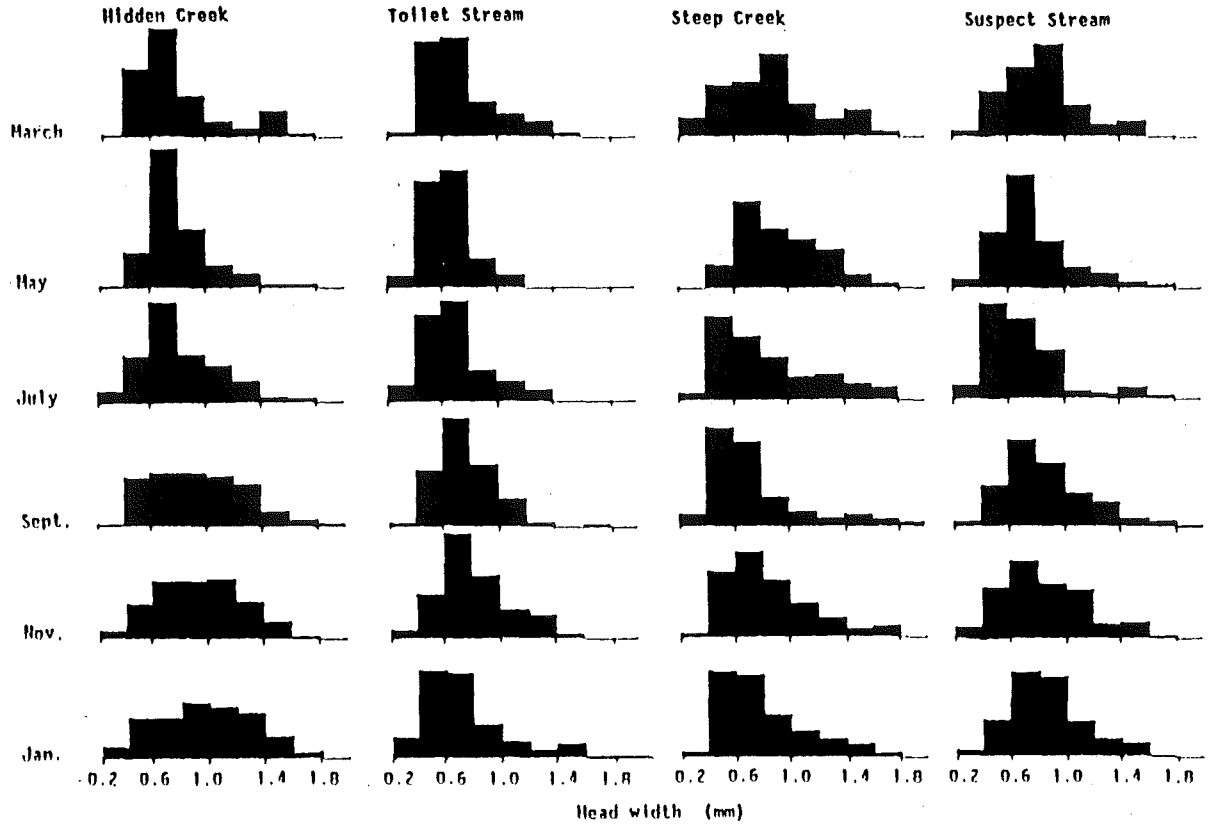


Figure 6.5. Size-frequencies of *Deleatidium* spp. larvae taken in 4-5 Surber samples on six dates in 1985-86 from four South Westland streams.

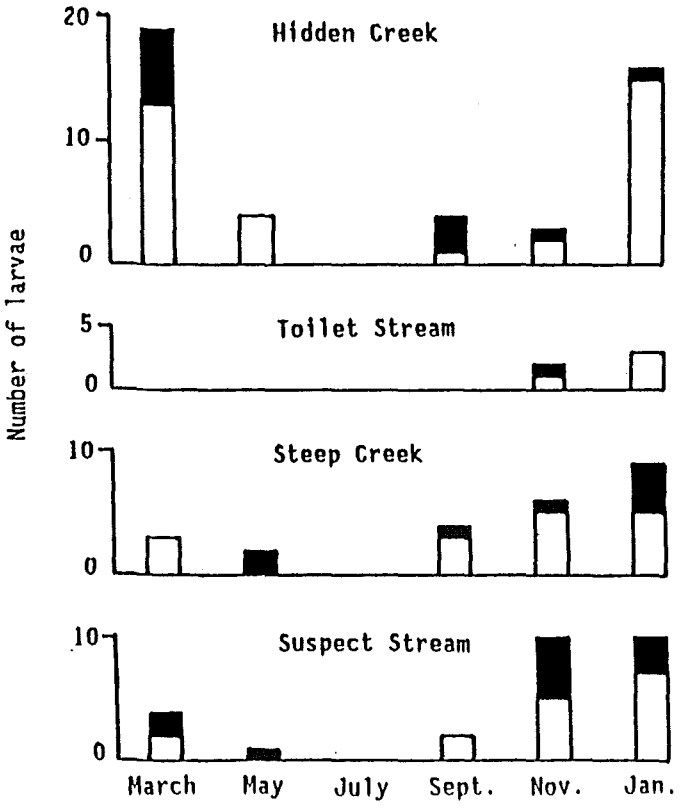


Figure 6.6. Numbers of final instar *Deleatidium* spp. larvae taken in 4-5 Surber samples from four South Westland streams on six dates in 1985-86. Shaded portions of histograms represent larvae with dark wing pads.

6.3.3. Gut Content Analyses

Guts of *Zelandobius confusus* larvae taken from both clearwater streams in November and May were empty, but in Steep Creek and Suspect Stream guts contained mostly fungal hyphae (39-72 %), FPM (23-36 %), as well as small quantities of SPOM (5-13 %) and MPOM (5-10 %) (Fig. 6.7.). Most of the fungi in *Z. confusus* guts (Plate 6.1.) were sooty moulds (Euantennariaceae and Metacapnodiaceae) which are terrestrial species that grow on honeydew excreted by scale insects infesting trees (Hughes, 1972), and would have entered the streams on allochthonous litter. Diatoms were common only in November (5 % of total contents) and only in guts of larvae from Steep Creek which had a relatively open canopy (see Section 2.3.2.).

Gut contents of *A. cyrene* were dominated by FPM at all sites except Suspect Stream where sooty mould fungi comprised 65 % of contents in November (Fig. 6.8.; Plate 6.1.). These fungi were seen in guts of Steep Creek larvae as well, but were not observed in larvae from the clearwater sites. SPOM and MPOM had been ingested by larvae at all sites, and were usually most common in Steep Creek where they comprised up to 18 % and 14 % of gut contents, respectively.

Gut contents of *Deleatidium* larvae collected from all sites in November and May were dominated by fine particulate matter (FPM) which represented 69-99 % of total contents (Fig. 6.9.; Plate 6.1.). The proportion of FPM was highest in larvae from Suspect Stream and lowest in Toilet Stream larvae on both dates. Diatoms were significantly more common (9-21 % of total contents) in guts of *Deleatidium* larvae from the clearwater streams than from Steep Creek (2-7 %) (t-test, $P < 0.05$; arcsine square root (x) transformed); no diatoms were recorded in guts of larvae from Suspect Stream. Filamentous algae were common (8-13 %) in guts of larvae from Steep Creek, but were rarely seen at other sites.

The guts of *S. maclellani* larvae taken from Toilet Stream in May were empty, but on other dates they contained mainly animal tissue (32-82 %) and FPM (17-66 %) at all sites (Fig. 6.10.). Significantly more animal material (mostly *Deleatidium*) and less FPM had been ingested in the clearwater than the brownwater streams where chironomids were the most abundant prey (t-test, $P < 0.05$; arcsine square root (x) transformed).

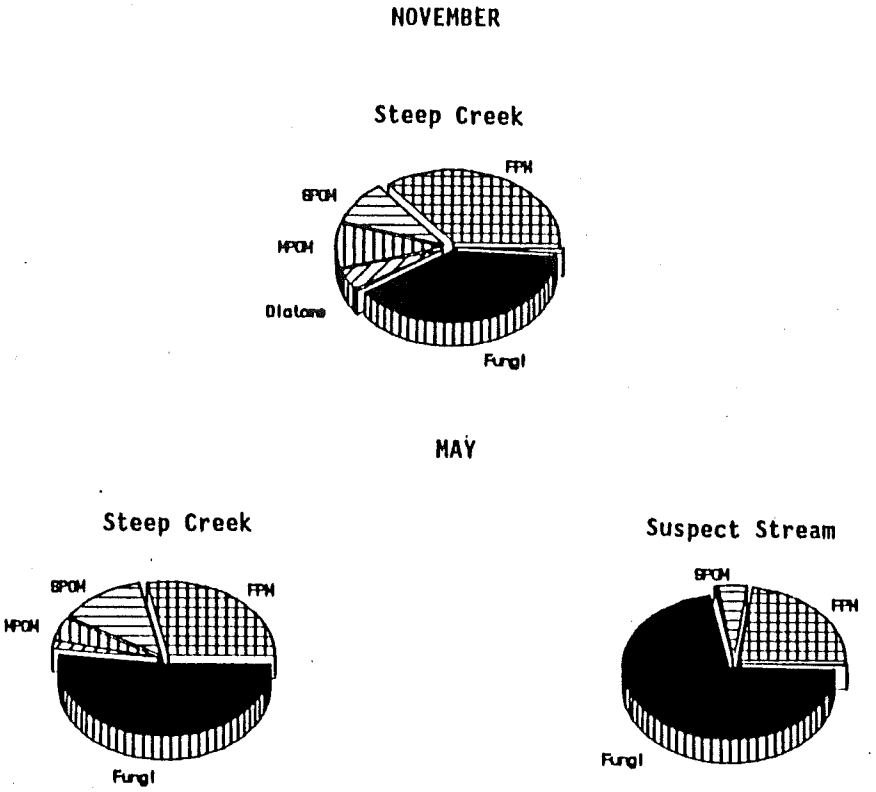


Figure 6.7. Percentages of eight food categories found in guts of *Zelandobius confusus* larvae from Suspect Stream (May 1987) and Steep Creek (November 1986 and May 1987). Only categories which comprised ≥ 5 % of total gut contents are labelled.

FPM - Fine particulate matter (< 75 μm)

SPOM - Small particulate organic matter (75 - 250 μm)

MPOM - Medium particulate organic matter (250 - 1000 μm)

Diatoms

Filamentous algae

Fungi

Animal

Other

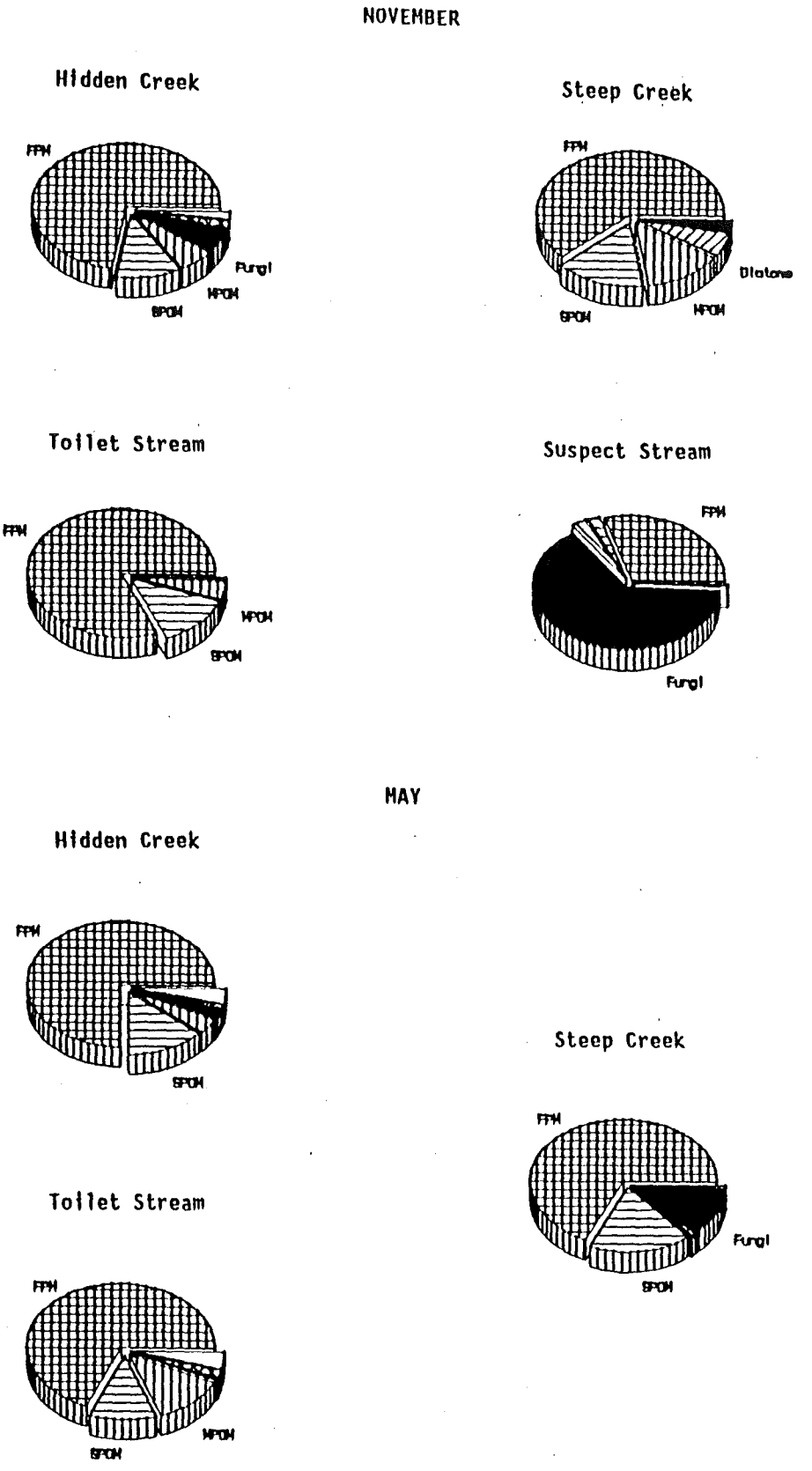


Figure 6.8. Percentages of eight food categories found in guts of *Austroperla cyrene* larvae collected in November 1986 and May 1987 from four South Westland sites. Conventions as for Figure 6.7.

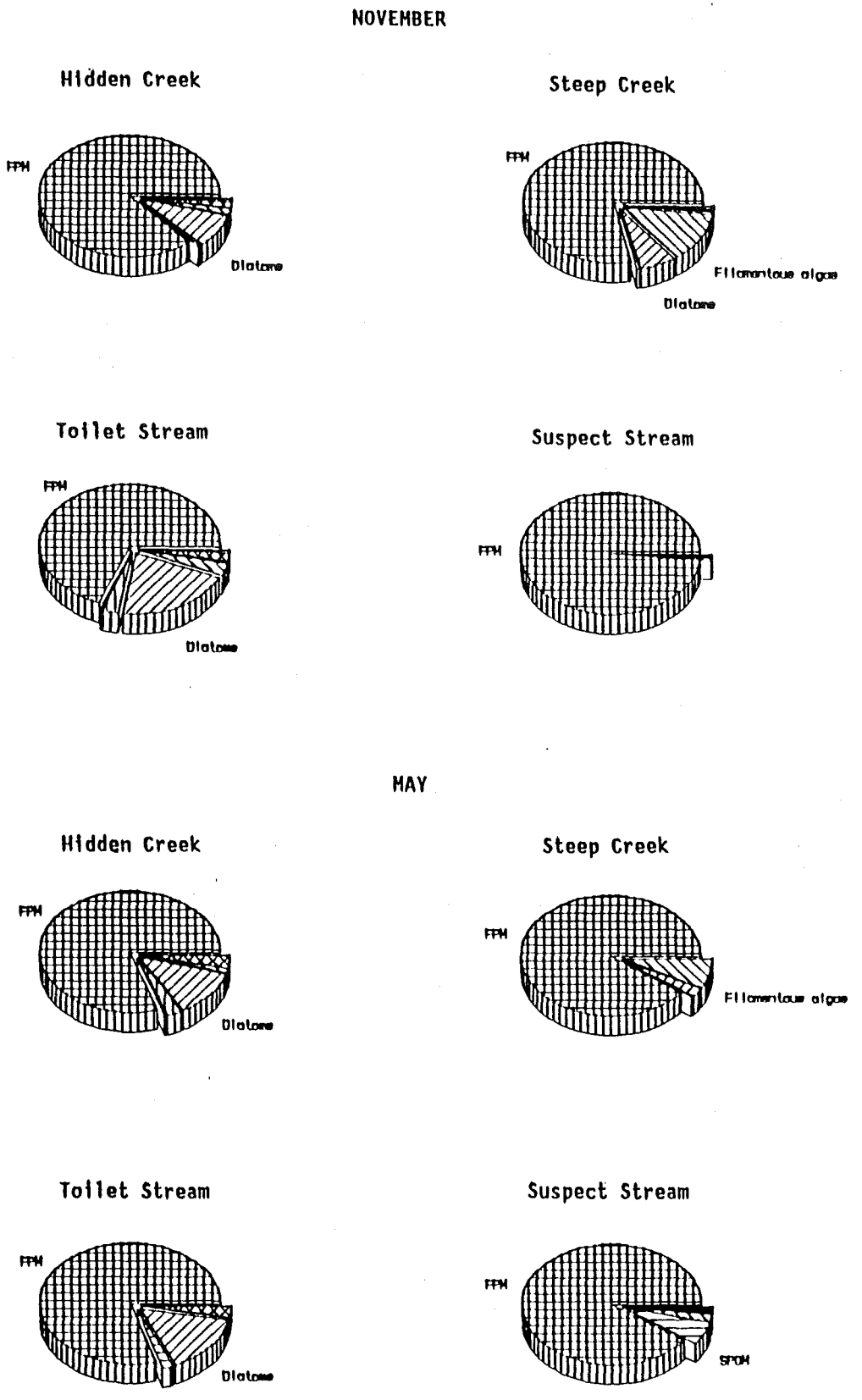


Figure 6.9. Percentages of eight food categories found in guts of *Deleatidium* spp. larvae collected in November 1986 and May 1987 from four South Westland sites. Conventions as for Figure 6.7.

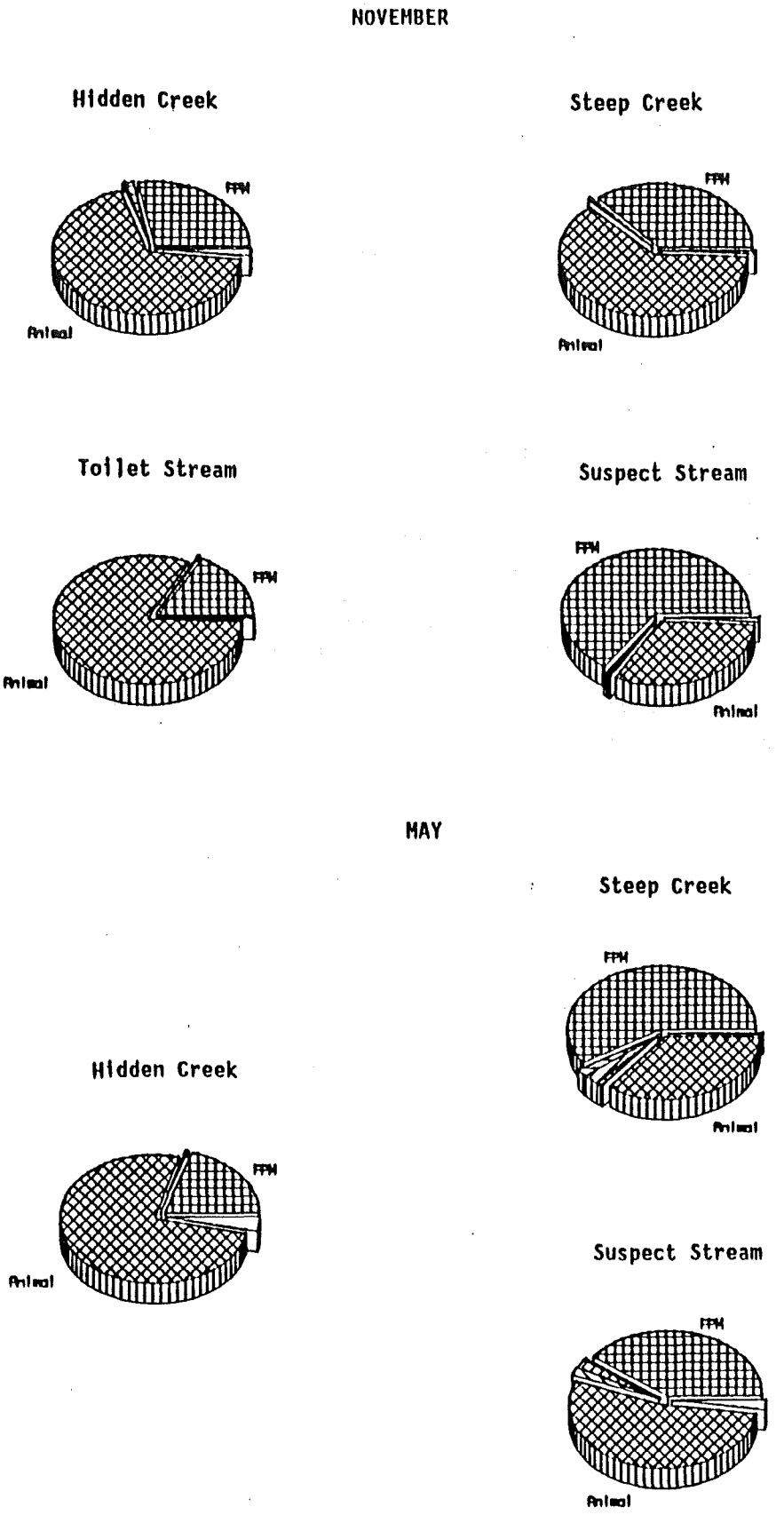
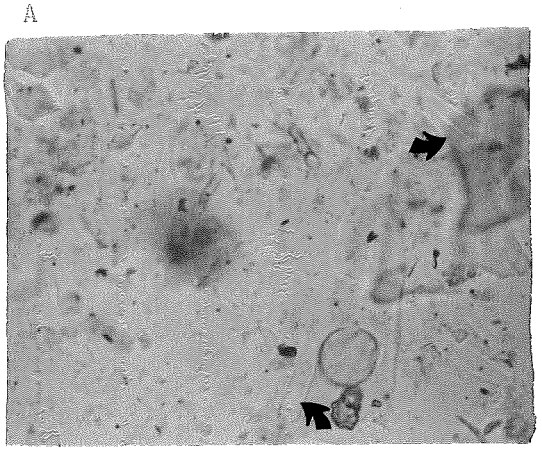


Figure 6.10. Percentages of eight food categories found in guts of *Stenoperla maclellani* larvae collected in November 1986 and May 1987 from four South Westland streams. Conventions as for Figure 6.7.

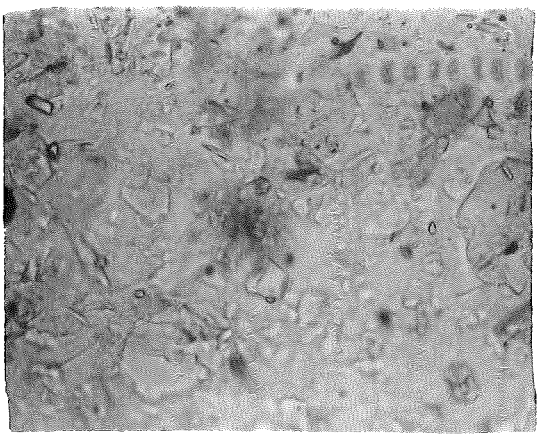
Plate 6.1. Light micrographs of gut contents of three invertebrate taxa collected in November 1986 or May 1987 from four South Westland streams. Guts of *Deleatidium* spp. larvae (A, B) were dominated by fine particulate matter (FPM) and diatoms (arrows) were also relatively common in larvae from the clearwater sites. *Zelandobius confusus* larvae from Steep Creek and Suspect Stream had ingested large amounts of sooty mould fungi (C, D) as had *Austroperla cyrene* larvae from the latter site (E). In contrast, *A. cyrene* larvae from the other sites (e.g., Hidden Creek; F) ingested predominantly fine, small organic and medium organic particulate matter (see Section 6.3.3.).

A, *Deleatidium* spp. from Toilet Stream in November. 400 x mag.
B, *D. lillii* from Steep Creek in November. 400 x.
C & D, *Z. confusus* from Suspect Stream in May. 40 x (C) and 100 x (D).
E, *A. cyrene* from Suspect Stream in November. 100 x.
F, *A. cyrene* from Hidden Creek in November. 100 x.

A

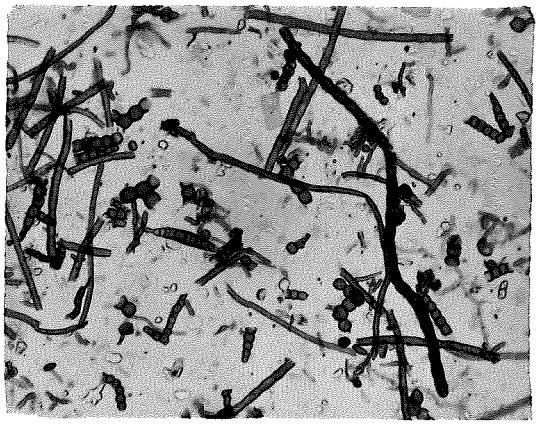


B

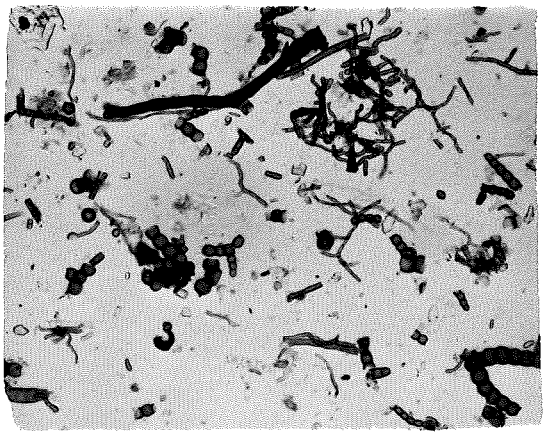


C

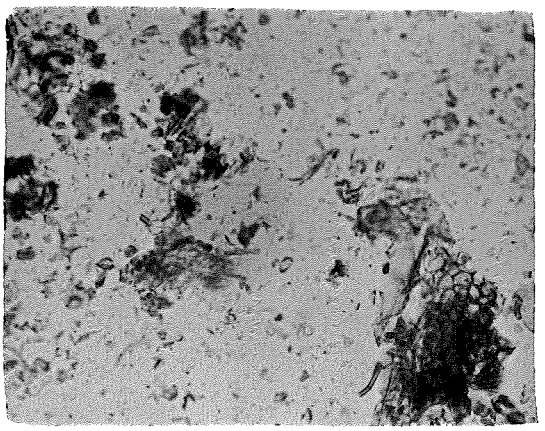
D



E



F



6.4. DISCUSSION

Invertebrate faunas of South Westland streams

Although the number of taxa collected on each sampling date was always higher in the clearwater streams, overall differences between sites in numbers of taxa in the various insect orders were small. This suggests that water chemistry did not have an over-riding effect on taxonomic richness at the four sites even though pH recorded in Steep Creek was as low as 4.3. All of the six most common taxa in the North Westland streams sampled (see Section 5.4.) were found at most, if not all, of the South Westland sites, and although *Ameletopsis perscitus* was found only at the brownwater sites, it is widespread in West Coast streams in general (Winterbourn & Collier, 1987). *Nesameletus* sp. larvae were collected only from the circumneutral, clearwater sites and were not found by Winterbourn & Collier (1987) in West Coast waters with pH < 5.0. In laboratory bioassays, *Nesameletus* sp. larvae survived at a mean pH of 4.2-4.3 up to ten days after which mortality rates were rapid but similar to those of larvae kept in circumneutral water (Appendix V).

Although differences in species richness between streams were small, total invertebrate densities were, on average, 2.4 to 4.8 times higher at the clearwater than the brownwater sites. Many factors are thought to affect invertebrate abundances in streams, and these can include current speed, substrate type, water temperature (Williams, 1981), food (Cummins & Lauff, 1969), degree of canopy cover (Hawkins *et al.*, 1982), predation by fish (Healey, 1984) and competition (Peckarsky, 1983). Differences in temperature or degree of canopy cover between streams were not consistent with higher densities at clearwater sites whereas fish were present only in the brownwater streams and fed mostly on terrestrial prey (Main & Lyon, in press). Although some changes in total invertebrate density in Hidden Creek and Toilet Stream could have reflected antecedent flow conditions, densities at these sites often were similar on equivalent dates even though flow variability and magnitude were considerably greater in Toilet Stream. Substrate particle size distributions were not assessed in this study, but Pfankuch (1975) stability ratings which take into account the proportion of stable bed materials and their degree of compactness were determined (see Table 2.2.). Stability ratings did not reflect patterns of invertebrate abundance among streams, but were related to temporal variability of the benthos such that fluctuations in density declined as bed stability increased. Temporal changes in abundance did not follow a seasonal pattern in any stream and there was a general lack of unison between

sites.

The only species which was present at all sites but was more abundant in Steep Creek and Suspect Stream was the stonefly *Zelandobius confusus*. Hildrew *et al.* (1984a) reported a similar phenomenon for some acidic streams in southern England where detritivorous stonefly densities were high even though total species numbers were low. They suggested that density compensation was occurring whereby reduced competition broadened niche width and enabled generalist stonefly species to attain high densities. In contrast, *Deleatidium*, *Austroperla cyrene*, *Stenoperla maclellani* and Oligochaeta, which were present at all sites, reached much higher densities in the clearwater streams. These taxa evidently were able to tolerate the acidic conditions in Steep Creek and Suspect Stream, but their success appeared to be limited by some factor(s) directly or indirectly associated with low pH (possibly food supply).

Life histories and population dynamics of Deleatidium

Size-frequency distributions revealed that *Deleatidium* populations at the four sites had poorly-synchronised life histories with most size classes present year round. All populations were dominated by small larvae on most dates indicating almost continual recruitment through delayed hatching or extended egg-laying. In this respect, life histories of South Westland *Deleatidium* populations resemble those studied by Winterbourn (1974) in the Selwyn and Scrimgeour (1987) in the Ashley, both lowland rivers in eastern South Island where hatching apparently occurred throughout the year and larvae of all sizes were present in most months. The presence of two or more species of *Deleatidium* with staggered life histories could partly explain the extended hatching periods and poorly-defined life histories in Hidden Creek and Toilet Stream. However, the same phenomena were observed at the two brownwater sites where gill morphology and abdominal pigmentation indicated that only one species was present.

Overall densities of *Deleatidium* larvae were 1.7-3.7 times higher at the clearwater than the brownwater sites, and were temporally least variable in the stream with the most stable bed and temperature regime (Hidden Creek). However, biomass in Toilet Stream was similar to that in Steep Creek and Suspect Stream, reflecting the greater abundance of smaller larvae at the former site. In contrast to the present study where no seasonal changes in biomass were evident, biomass of *Deleatidium* larvae in Lake Grasmere, near Cass (Greig, 1976), and in Selwyn River (Winterbourn, 1974) was highest in summer when large numbers of final instar larvae were present.

No significant differences in sizes of male and female *Deleatidium* larvae were found in the present study. However, Winterbourn (1974) and Greig (1976) reported that females were slightly smaller than males, whereas Towns (1983b) found that females of *Deleatidium* sp. A were larger than males in Waitakere Range streams. Sweeney (1984) suggested that larval maturation size was affected primarily by the quality of available food. Although mean sizes of final instar larvae were greater at the clearwater than the brownwater sites, no conclusions regarding food quality can be drawn from this because there was considerable variation in final instar sizes at all sites (largest individuals in fact were collected from Suspect Stream), and different species, which at present are indistinguishable as larvae (Winterbourn & Gregson, 1981), were almost certainly present at brownwater and clearwater sites.

Most estimates of annual *Deleatidium* production in streams and lakes are less than 10 g dry weight.m^{-2} (e.g., Winterbourn, 1974*; Greig, 1976; Hopkins, 1976), although Scrimgeour (1987) recorded production of 44.49 $g.m^{-2}.y^{-1}$ in a riffle in Ashley River. Thus, *Deleatidium* production in Hidden Creek (10.35 $g.m^{-2}.y^{-1}$) is amongst the highest recorded for *Deleatidium* and was 2.7 to 4.2 times higher than at any of the other three South Westland sites. Even so, my values are likely to be underestimates because not all small larvae were collected by the 0.5 mm mesh net, a limitation which is unlikely to have led to an error any greater than 10 % (Clifford *et al.*, 1979). The fairly stable flow and temperature regimes in Hidden Creek should have provided a relatively benign habitat (*sensu* Peckarsky, 1983) which appears to be reflected in the comparatively low larval mortality and high productivity of *Deleatidium* larvae at this site. In contrast, low bed stability and more variable flow and temperature regimes appear to have limited production of *Deleatidium* larvae in the other streams where few larvae were found in late instars. This may have been compounded at the brownwater sites by poor quality food, particularly in Suspect Stream which had a more stable bed but lower *Deleatidium* production than Steep Creek.

*, revised calculations indicate that the correct production estimate for this study was 19.57 $g.m^{-2}.y^{-1}$.

Diets of key taxa

Gut contents of *Deleatidium*, *A. cyrene*, *Z. confusus* and *S. maclellani* were examined to investigate whether differences in densities between brownwater and clearwater sites could be related to the nature of material ingested. Although high relative abundance of an item in the digestive tract does not prove its nutritional importance, it does implicate it as a major source of nourishment and gives clues to the principal feeding sites of different taxa.

Sooty mould fungi dominated gut contents of *Z. confusus* in Steep Creek and Suspect Stream where larval densities were much higher than at the clearwater sites. These fungi were also consumed by larvae of *A. cyrene* at the brownwater sites, but this species was more abundant in Hidden Creek and Toilet Stream where sooty mould did not colonise riparian vegetation. Sooty mould fungi were probably consumed while eating leaf material and this feeding activity presumably generated the fairly large proportions of MPOM, SPOM and FPM found in *A. cyrene* guts.

The larvae of *S. maclellani* preyed predominantly on chironomids in Steep Creek and Suspect Stream, but *Deleatidium* larvae were the main prey at the clearwater sites where they were more abundant. Winterbourn *et al.* (1984) found that larvae of *Stenoperla prasina* fed predominantly on *Deleatidium* and to lesser degrees on chironomids and small stoneflies in Devils Creek, a circumneutral clearwater stream in North Westland. In other studies, filamentous algae and detritus have been recorded in *Stenoperla* guts (Winterbourn, 1974; Winterbourn, 1982; Winterbourn & Rounick, 1985), suggesting that larvae of this taxon can be opportunistic feeders. FPM was abundant in *S. maclellani* guts at most South Westland sites, although some of this could have come from prey digestive tracts which may be important sources of predator nutrition (Cummins, 1973). Overall, *S. maclellani* guts from the clearwater sites contained proportionately more animal material (69-82 % of gut contents) than larvae from the brownwater sites (32-62 %), suggesting that limited prey availability and the absence of high quality alternative foods may limit densities of *S. maclellani* larvae in the brownwater streams.

Deleatidium guts were dominated by fine particles at all sites, diatoms were ingested in Hidden Creek, Toilet Stream and Steep Creek, and filamentous algae were also consumed at the latter site. Surprisingly, more diatoms were ingested by larvae from Toilet Stream than Hidden Creek where the stream bed was more exposed to direct sunlight. Winterbourn *et al.* (1984) found that 99 % of *Deleatidium* gut contents in Devils Creek, North Westland, were fine particles < 75 μm, apparently mostly of terrestrial origin.

Differences in densities of *Deleatidium* at the four sites could have been influenced by differences in the nutritive quality of epilithic FPM (discussed further in Chapter 7).

Several workers have expressed responses of benthic assemblages to acidification in terms of changes in functional feeding group representation, and interpreted this to reflect alterations in the type or quality of food available (e.g., Hall *et al.*, 1980; Otto & Svensson, 1983; Townsend *et al.*, 1983; Mackay & Kersey, 1985). However, the accuracy of functional feeding group classifications has been questioned by Hawkins *et al.* (1982) who suggested that food and feeding methods of most aquatic insects are likely to be more varied than such groupings acknowledge. I have not presented my results in terms of functional feeding group representation because several studies (see Winterbourn *et al.*, 1984 and references therein) have indicated that many members of New Zealand stream invertebrate faunas are herbivore/detritivores which can not be assigned reliably to shredder, scraper or collector/grazer guilds.

CHAPTER 7

COMPOSITION, STRUCTURE AND GRAZING OF

EPILITHON IN SOUTH WESTLAND

STREAMS

7.1. INTRODUCTION

Stone surface organic layers in streams (epilithon) typically are composed of an interwoven matrix of slime, fungi, bacteria, algae and fine particulate matter, and represent a potentially important food source for many stream invertebrates (Madsen, 1972; Rounick & Winterbourn, 1983a; Winterbourn *et al.*, 1985). Most Northern Hemisphere studies into the effects of acidification on epilithon have revealed an increase in algal biomass with decreasing pH (Hendrey, 1976; Hall *et al.*, 1980; Müller, 1980; Allard & Moreau, 1985; Mulholland *et al.*, 1986). Reasons proposed for the increase include lower grazing pressure by invertebrates, a successional shift to acid tolerant algal species, and reduced microbial decomposition of periphyton (Hendrey, 1976; Hall *et al.*, 1980). In contrast to the studies mentioned above, Maurice *et al.* (1987) recorded lower periphytic biomass in experimentally acidified Michigan streams, apparently as a result of lower nutrient availability and elevated metal (aluminium and/or iron) concentrations, whereas Tease & Coler (1984) found that low pH alone was sufficient to eliminate algae in waters acidified by coal leachates. Few workers have investigated responses of other components of epilithon to acidification, although Palumbo *et al.* (1987b) studied epilithic bacterial communities in some acidic Tennessee and North Carolina streams, and found that bacterial biomass and productivity were correlated positively with water pH.

In New Zealand streams, many invertebrates occur predominantly on stony substrata and organic layers on stone surfaces appear to be their main feeding sites (Winterbourn *et al.*, 1981; Rounick & Winterbourn, 1983a). Differences in the composition and structure of epilithon between streams therefore might be expected to influence densities and productivity of benthic invertebrates, in particular those of *Deleatidium* (Ephemeroptera: Leptophlebiidae) larvae which feed on stone surfaces and occur in many New Zealand streams (Rounick & Winterbourn, 1983a).

I investigated the biological and chemical composition of epilithic communities in two acid brownwater streams and two circumneutral clearwater streams in South Westland (see Fig. 2.3.) to determine whether differences in epilithon might contribute to the lower invertebrate densities observed at the acid sites. In addition, I measured rates of ingestion by *Deleatidium* larvae of epilithon from an acid and a circumneutral stream.

7.2. METHODS

7.2.1. Field Sampling

Equipment and sampling protocol

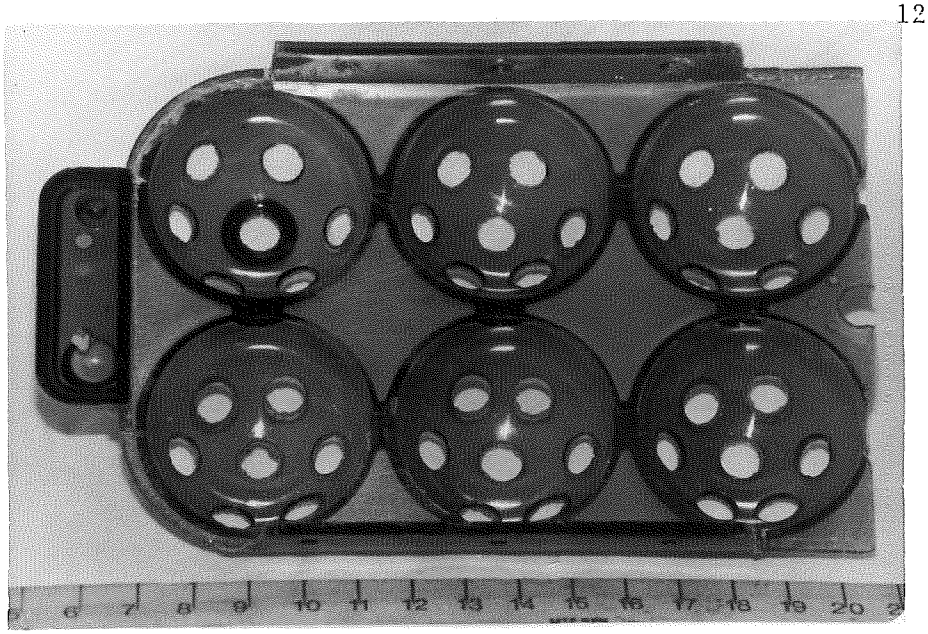
On 22-25 January 1985, wire-framed "baskets" covered with 7 mm plastic mesh (30 x 30 cm square, 11 cm deep) were filled with gravel and embedded in the stream beds of Hidden Creek, Toilet Stream, Steep Creek and Suspect Stream to provide stable attachment points for other experimental equipment (Plate 7.1.). Perspex egg trays were perforated to permit throughflow of water and were attached to baskets to accomodate experimental substrata (six greywacke river stones and one carbon rod). Trays were covered with thin plastic netting (20 mm mesh) to prevent stones washing away during high flows. Triangular pieces of perspex each drilled with two holes were secured to the downstream corners of all baskets to house scanning electron microscope (SEM) stubs on which stone chips were mounted (Plate 7.1.).

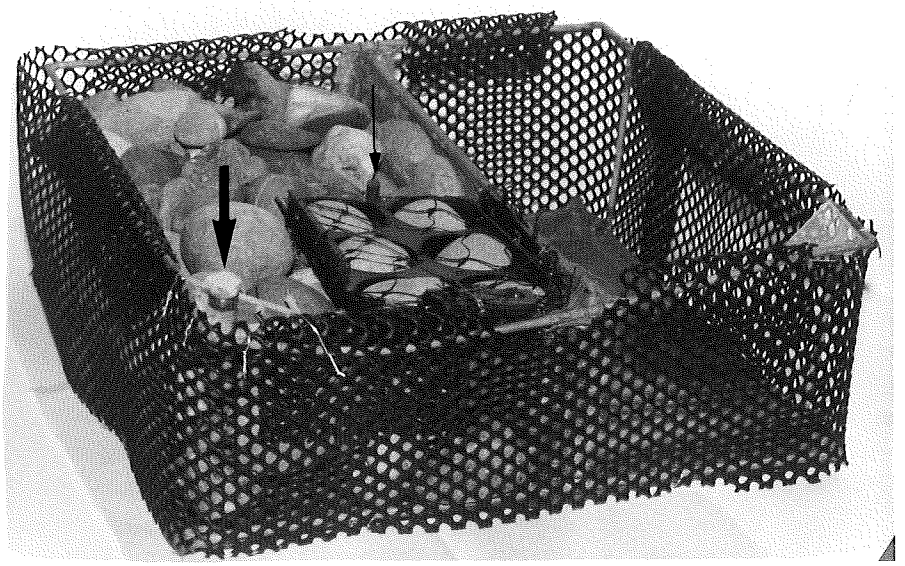
Stones were collected from the stream beds at the four South Westland sites for measurements of epilithic organic carbon on 22-25 January 1985, concurrently with the introduction of experimental equipment and substrata. Subsequently, stones from the trays and SEM stubs were removed for analysis and replaced with clean (chromic acid washed) substrata at approximately two monthly intervals until the main sampling program was terminated in January 1986. Epilithon grazing experiments were conducted in November 1986 and May 1987.

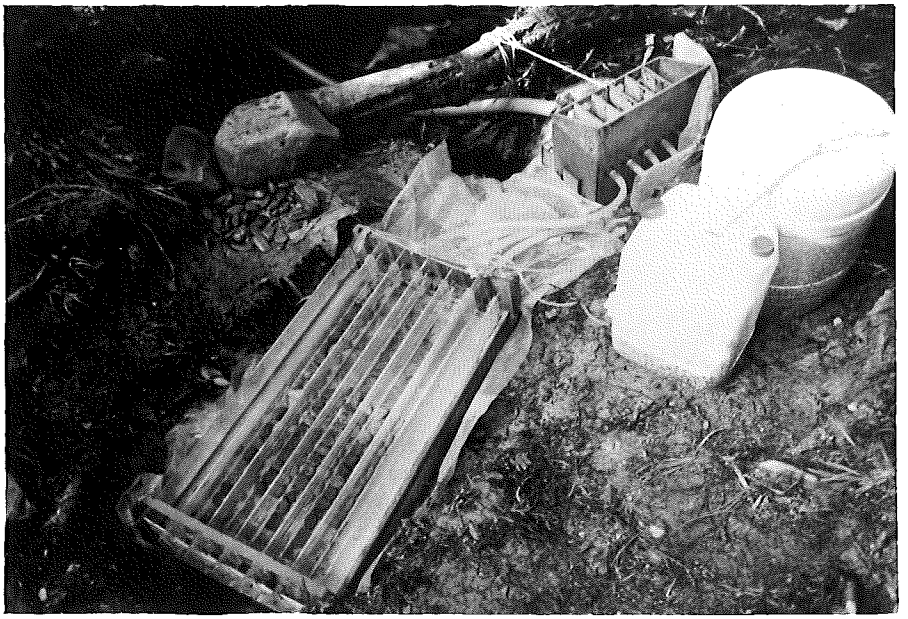
Electron microscopy

Greywacke stone chips were glued with Bostik^{R} to SEM stubs which were placed in stub holders attached to baskets in the streams (Plate 7.1.). Two stubs were oriented face-up and two face-down in each stream. After two months, stubs were removed, stored in 5 % gluteraldehyde in phosphate buffer and replaced with new stubs on which clean stone chips were mounted. Colonised stubs were rinsed twice in phosphate buffer, dehydrated in an alcohol series (Rounick & Winterbourn, 1983a), and air-dried. After coating with 50 nm of carbon/gold palladium, stone surfaces were viewed with a Cambridge Steroscan MK II SEM at magnifications up to 10000 times.

Plate 7.1. Experimental equipment used for analysis of epilithon in four South Westland streams. Upper photo shows perforated, plastic stone trays which permitted throughflow of water (scale bar = cm). Middle photo shows "baskets" (30 x 30 cm) containing stone trays, a carbon rod (thin arrow) and a SEM stub (thick arrow). Bottom photo shows experimental stream channels (105 cm long) containing artificial substrata in position at Steep Creek (see Appendix VI). Two solutions of KOH were piped from the white containers into two channels to elevate water pH, whereas water in a third channel was unmodified.







Energy dispersive X-ray analysis (EDAX)

The elemental composition of epilithic communities at the four sites was determined using EDAX coupled to the SEM. This technique identifies which elements are present according to the wavelengths of X-rays emitted, and the numbers of emissions (per second) provide a semi-quantitative assessment of elemental abundance.

Carbon rods (5 mm diameter, 10-15 mm long) were attached to trays (Plate 7.1.) at the four sites on two occasions (March and September 1985) and, after about two months (May and November, respectively), were removed, air-dried and stored in dust-proof containers. Before analysis with an EDAX 9100 system, rods were mounted on SEM stubs with carbon paste and coated with 50 nm of carbon. Randomly selected areas (n = 5 per sample) of rod surface and individual components of the periphyton (diatoms and algal filaments) on which no mineral particles could be seen were analysed. Readings were normalised against a blank carbon rod so that only emissions from material which had accrued on rod surfaces since their introduction into the streams were counted. Fields were analysed for 60 (May) or 100 (November) seconds with the system set at 20 kV, 50 μm aperture and spot size 6.

Respiration and primary production

After removal from trays, stones were placed in stream water in a specially constructed perspex carrying box consisting of two tiers, each with six compartments (one per stone) designed to prevent epilithic layers abrading during transport. Stones were kept as cool as possible until respiration experiments could be started at the field base (up to six hours later).

Six stones from each site were placed in clean (chromic acid washed) glass jars (volume 110 m*l*) and water collected from the same stream was decanted carefully into these so as not to disturb the epilithon. Six jars containing water but no stones served as controls. Filled jars were closed with rubber bungs and any remaining air was evacuated through syringe needles which were then sealed with parafilm.

Stones were incubated in dark and then light conditions inside a closed, white wooden box (60 cm long, 25 cm wide, 28 cm deep). For dark incubations the box was lined with black PVC, but this was removed for light incubations which were carried out under a 20 watt Atlas artificial daylight tube fitted inside the lid. Incubation temperatures were kept as close as possible to ambient stream temperatures (usually $\pm$ 5^{o}C), and

whenever necessary water piped from a nearby lake was circulated through the box to keep jars cool. After 10-16 hours incubation, the amount of oxygen consumed or produced in jars with and without stones was measured using a YSI Model 54 meter and probe.

Values were adjusted for respirometer volume and expressed as μl oxygen consumed (community respiration) or produced (net primary production) relative to controls per cm^2 of stone surface per hour (see following section for description of surface area measurement methods). Stones were frozen until TOC or photosynthetic pigment concentrations could be measured.

Organic carbon analyses

Total organic carbon (TOC) was measured using heat-by-dilution dichromate oxidation as described in Section 3.2.1. Stones were placed in 100 m*l* beakers and organic matter was oxidised with 1 N potassium dichromate. After cooling, the acid/dichromate mixture was rinsed into 250 m*l* flasks with 150 m*l* distilled water and titrated with 1 N ferrous sulphate following addition of phosphoric acid and indicator. Organic carbon was calculated using Equation 3 in Section 3.2.1. and expressed in terms of stone surface area (range 20-40 cm^2). This was measured by wrapping stones in aluminium foil of known weight per unit area.

Photosynthetic pigment analyses

Chlorophyll *a* and pheophytin *a* were measured on stones (frozen following oxygen measurements) taken from streams in September and November 1985 and January 1986, and not used for TOC analyses. Stones were immersed in 90 % acetone (15-50 m*l* depending on size and shape of the stone) and pigments were extracted overnight in the dark at 4^oC. Extract absorbances were read at 410, 430, 665 and 720 nm against a solvent blank on a Pye Unicam SP 1800 spectrophotometer and concentrations (per unit stone suface area) of chlorophyll *a* and pheophytin *a* were calculated by the method of Moss (1967a, b). Percent pheophytin was calculated using the 430:410 absorbance ratio-graphical technique and a standard curve based on average values of algal communities given by Moss (1967a).

7.2.2. Epilithon Grazing and Preference Experiments

Deleatidium *grazing rates*

The amount and composition (organic/inorganic) of material grazed from streambed stones by *Deleatidium* larvae were measured to compare consumption rates of epilithic layers from a brownwater and a clearwater stream. Trials were run in November 1986 and May 1987 using identical experimental procedures. Fifteen stones of similar size were collected from Hidden Creek and Steep Creek, and placed in 250 m*l* tubs containing water from the same stream. Additional stones (10 per site) were collected, kept cool in the dark, and later frozen for TOC or photosynthetic pigment (Kontron Uvicon 860 spectrophotometer) analyses. *Deleatidium* larvae (300-400 per site) were collected concurrently and taken to the field base in water-filled plastic containers.

All samples were kept cool (5^{o}C) until experiments were begun (within six hours of sample collection). Stones and larvae were arranged in six combinations (1 stone and 9-15 larvae per tub; five tubs per combination) as follows:

1) Hidden Creek stones and larvae;
2) Hidden Creek stones, Steep Creek larvae;
3) Hidden Creek stones, no larvae;
4) Steep Creek stones and larvae;
5) Steep Creek stones, Hidden Creek larvae;
6) Steep Creek stones, no larvae.

Trials were conducted in filtered (GF/C) water from the same stream as the larvae or, in trials without larvae, from the same stream as the stones. In May, larvae from each site were kept with water from that site but with plastic mesh instead of stones to determine the amount of faeces produced when feeding was prevented. All larvae were allowed to feed in the dark for 41-48 hours at 12-16^{o}C.

At the end of the experiments, larvae were removed, preserved with 10 % formalin, dried (50^{o}C) and weighed (0.1 mg). Stones were removed from tubs and grazed material (faeces and other fine particulates) was collected on pre-ashed and pre-weighed GF/C filters. Filters and grazed material were dried, weighed, ashed and reweighed to estimate amounts (total and inorganic) of material present. The weight of organic material was obtained by difference. Blank filters subjected to all the above procedures were used to make any adjustments that were necessary as a result of changes in filter weight.

7.3. RESULTS

7.3.1. Structure and Biological Composition of Epilithon

Hidden Creek (Plate 7.2.)

Electron microscopy showed that surfaces of stone chips oriented upwards in Hidden Creek were colonised predominantly by the diatoms *Gomphonema subclavatum* and *Achnanthes minutissima*, and by a blue-green alga (*?Chamaesiphon* sp.) which often carpeted stone surfaces beneath diatoms. *?Chamaesiphon* sp. was most abundant in summer (March and November 1985, January 1986) whereas another diatom *Cocconeis placentula*, which was usually uncommon, was relatively abundant in July. Other less common diatoms found in Hidden Creek were *Achnanthes linearis* and a species of *Fragilaria*. Filaments of a cyanophyte, *?Lyngbya* sp., occurred frequently between diatoms and in crevices, and patches of another blue-green, *?Merismopedia* sp., were seen occasionally (e.g., in May).

Bacteria often occurred on upper surfaces of stones in Hidden Creek, but fungi appeared to be uncommon. Epilithic layers at this site were generally free of non-cellular material, but in May and September large amounts of amorphous material were visible.

Toilet Stream (Plate 7.3.)

Diatom densities were generally lower on upper surfaces of stone chips from Toilet Stream than Hidden Creek. In Toilet Stream, *A. minutissima* was the most abundant diatom with *Achnanthes lanceolata* and some *Cocconeis*, *Gomphonema*, *Synedra*, *Fragilaria* and possibly *Eunotia* species less common and often patchily distributed. *?Chamaesiphon* sp. was also present in Toilet Stream but in much lower densities than in Hidden Creek.

Bacteria and threads of fungi and/or Actinomycetes were seen regularly on upper stone surfaces in Toilet Stream and often they were embedded in a matrix of mucilage. Epilithic layers were generally free of amorphous material, but in September, accumulations similar to those seen in Hidden Creek on the same date were evident.

Steep Creek (Plate 7.4.)

Filamentous algae including *Tribonema* sp. (Chrysophyta) and *Stigeoclonium* sp. (Chlorophyta) were usually present on the upper surfaces of stone chips in Steep Creek. On most dates, only a few isolated strands

were seen, but in March, algal filaments formed a relatively dense covering. Diatoms were not as common at this site as in Hidden Creek, although *Fragilaria ?vaucheriae* and two species of *Eunotia* (*E. curvata* and an unidentified form) were sometimes abundant, especially in May. *Fragilaria virescens*, *Synedra ?ulna* and a creeping blue-green alga (*?Tolypothrix* sp.) occurred in Steep Creek but were rare.

Few bacteria and fungi were seen on upper stone surfaces in Steep Creek although rods and spherical objects (possibly bacteria) were seen in May and June. Filaments of fungi or Actinomycetes were abundant in January whereas accumulations of amorphous material were found on most dates and were particularly extensive in May.

Suspect Stream (Plate 7.5.)

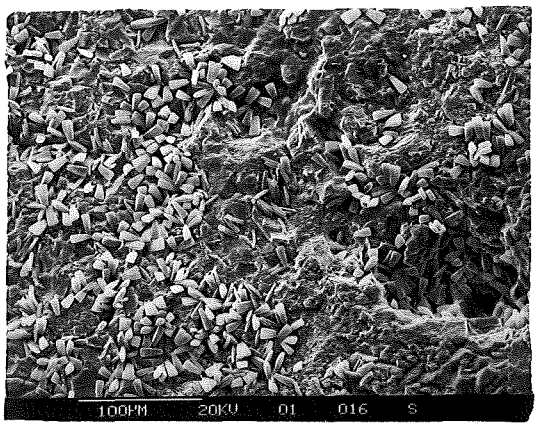
In March, surfaces of stone chips oriented upwards in Suspect Stream were covered by a thick layer of mucilage interwoven with threads. On other dates, a few scattered diatoms (mostly *Fragilaria* and *Eunotia* spp.) and filamentous algae were seen, and these were most common in November. *?Tolypothrix* was observed only in July. Bacteria were not abundant on any date but deposits of amorphous material were common.

Epilithon on under-surfaces of stones (Plate 7.6.)

Lower surfaces of stone chips were colonised predominantly by bacteria, fungi and actinomycete-like filaments, although the degree of colonisation varied widely between sites and dates. Fungal hyphae were common in Hidden Creek in May but were seen rarely on other dates. In contrast, filaments and bacteria were characteristic colonists of downward facing stubs in Toilet Stream and sometimes they were associated with mucilaginous layers over stone surfaces (e.g., in January). Structurally similar layers were also seen in Suspect Stream in January, but otherwise the undersides of stones in that stream were coated lightly with amorphous material only. Some filamentous algae grew on lower surfaces of stone chips in Steep Creek (mostly in May) indicating that they received some incidental light. High densities of coccoid bacteria were found in Steep Creek in May, but generally bacterial densities at that site were low.

Plate 7.2. Scanning electron micrographs of epilithon colonising stone chips facing upwards in Hidden Creek. Diatoms present were mostly *Gomphonema subclavatum* (e.g., B) and *Achnanthes minutissima* (E) although *Cocconeis placentula* (F) was relatively common in July. Filaments of *?Lyngbya* sp. (C) also were seen. Another blue-green (*?Chaemosiphon* sp.) is visible in the background and was particularly common in November (D). Deposits of amorphous material were evident in May (B) and September.

A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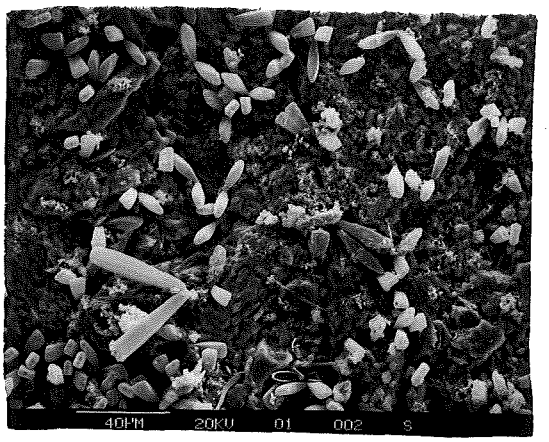
B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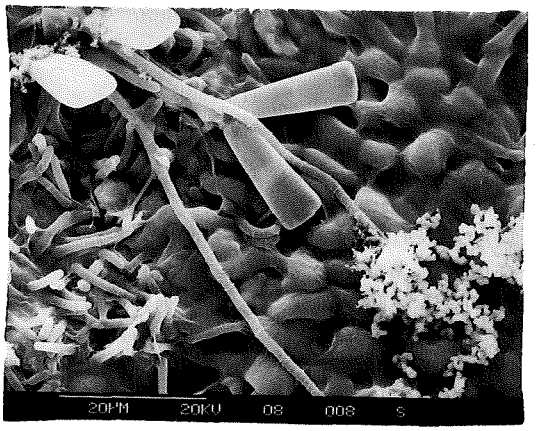
C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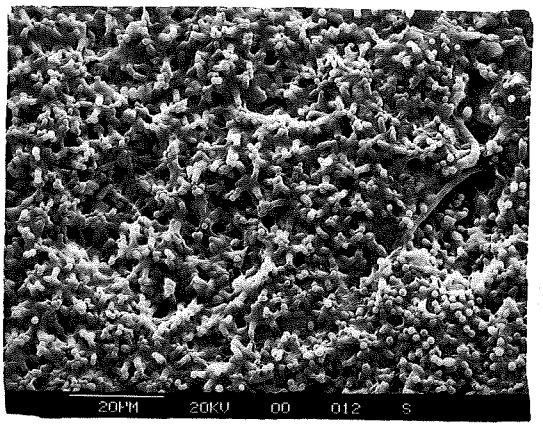
D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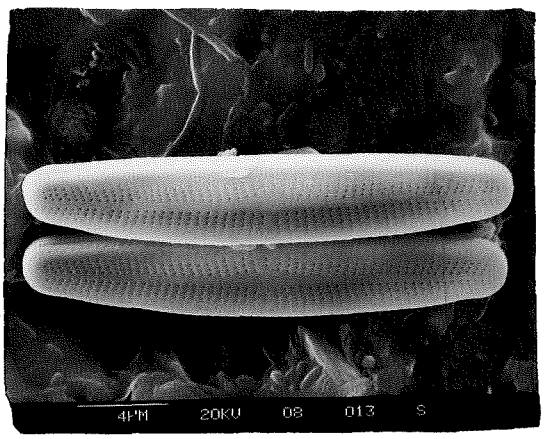
E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F

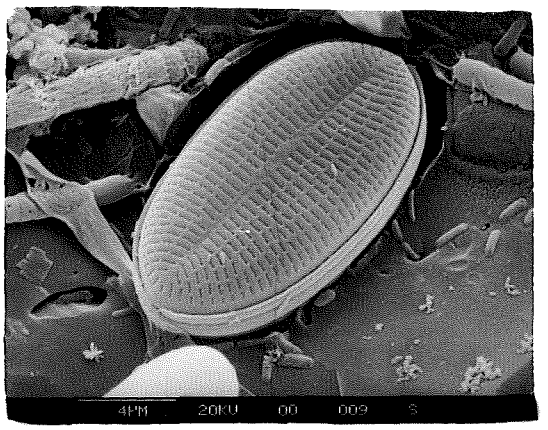
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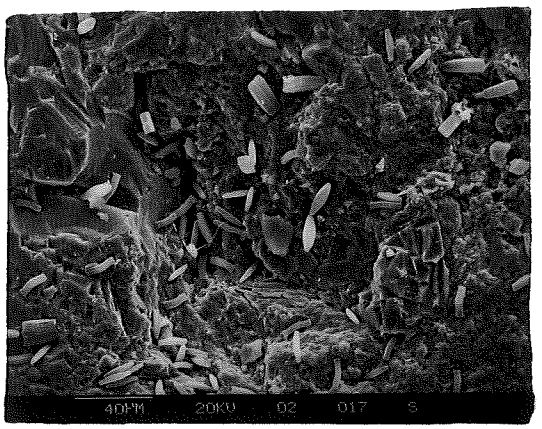
Plate 7.3. Scanning electron micrographs of upper surfaces of stone chips incubated in Toilet Stream. The commonest diatom at this site was *A. minutissima* (B & D), although *Gomphonema* (A), some *Fragilaria* (thick arrow; C), *Synedra* (thin arrow; C) and possibly *Eunotia* (arrow; B) species were also seen. Bacteria (E & F) were observed regularly as were fine filaments (?Actinomycetes) which sometimes covered daitoms (D). Amorphous material was common in September only (B & C).

A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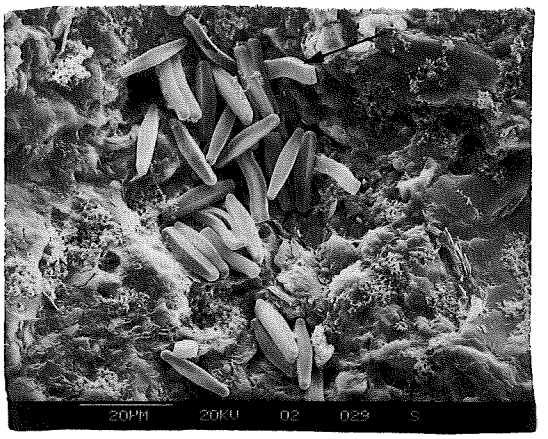
B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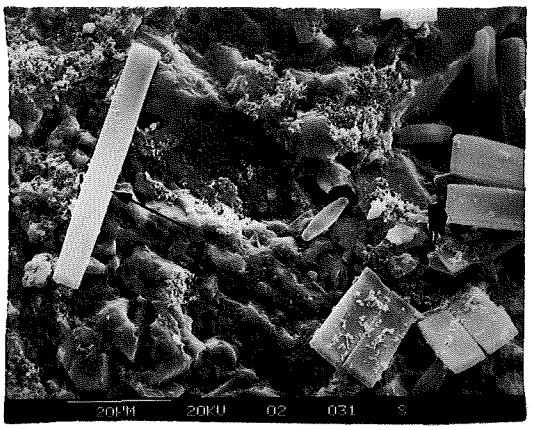
C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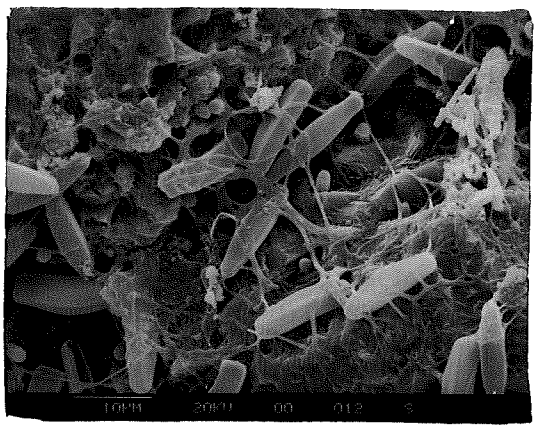
D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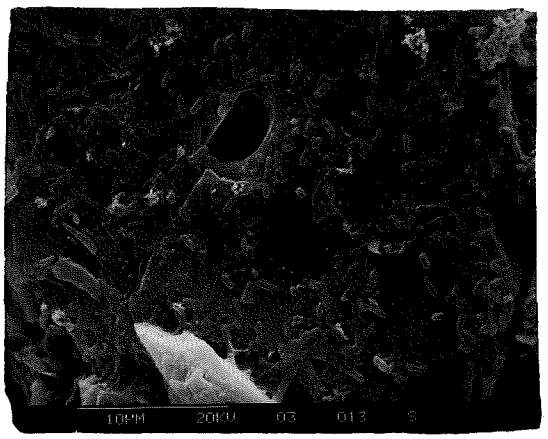
E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F

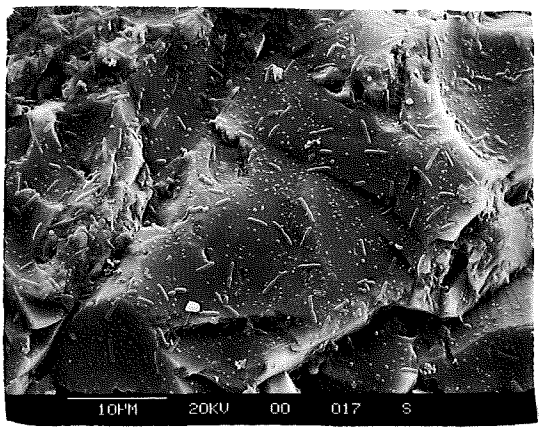
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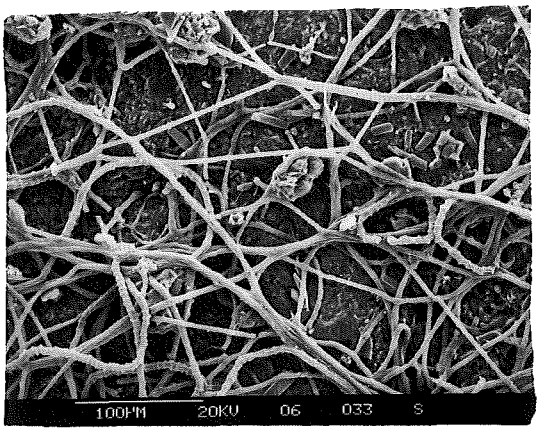
Plate 7.4. Scanning electron micrographs of epilithon colonising stone chips facing upwards in Steep Creek. Filamentous algae were common in March (A) but were less abundant on other dates (e.g., B (May) & C (January)). *Fragilaria ?vaucheriae* was the most common diatom (D), although *Eunotia curvata* (F) and *Eunotia* sp. were also evident. Amorphous material was often seen on stone surfaces at this site (e.g., B, D, E & F).

A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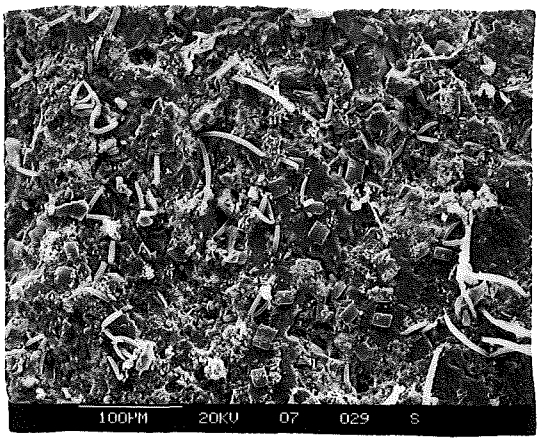
B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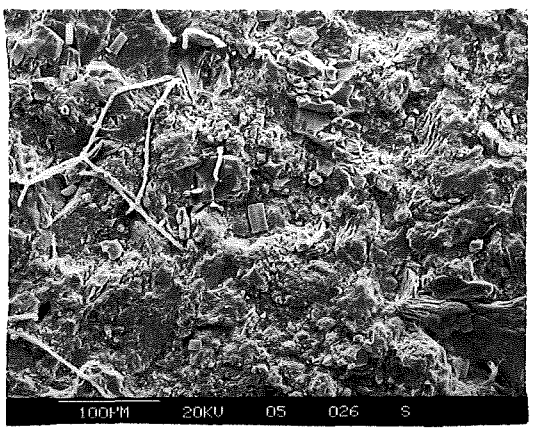
C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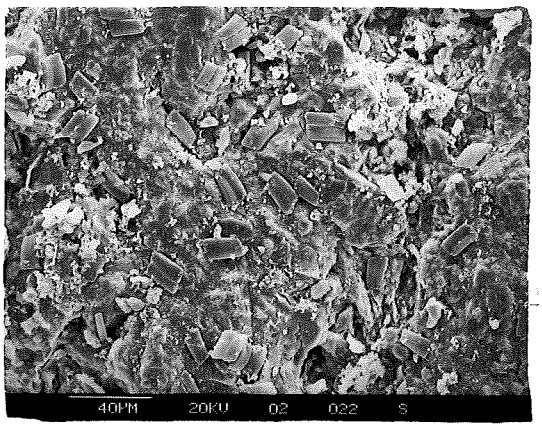
D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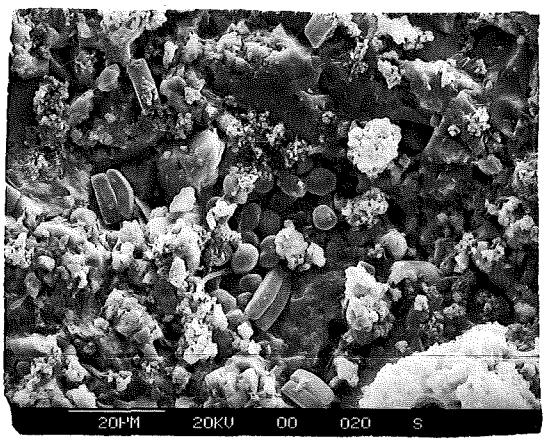
E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F

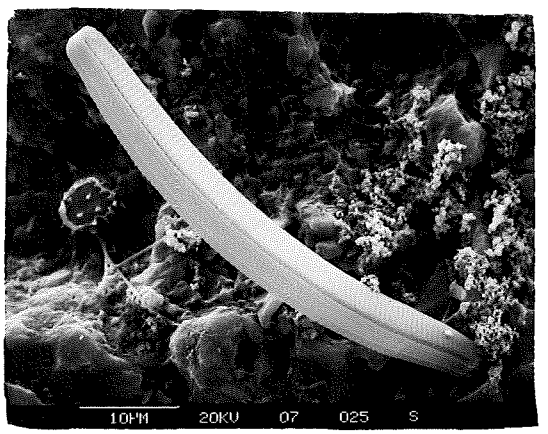
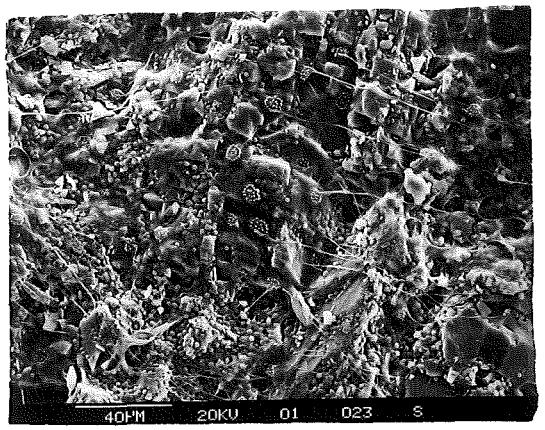

10PM 20KV 07 025 S

Plate 7.5. Scanning electron micrographs of upper surfaces of stone chips incubated in Suspect Stream. Surfaces were covered by mucilage and filamentous organisms in March (A & D), but on other dates only a few diatoms (e.g., *Eunotia* sp. in F) or filamentous algae (e.g., *?Tolypothrix*, B) were seen. In A, crown-like structures were associated with threads (fungi or Actinomycetes); spherical objects (see arrow in F) may be blue-green algae. Amorphous material was common on most dates (e.g., C (January) & E (May)).

A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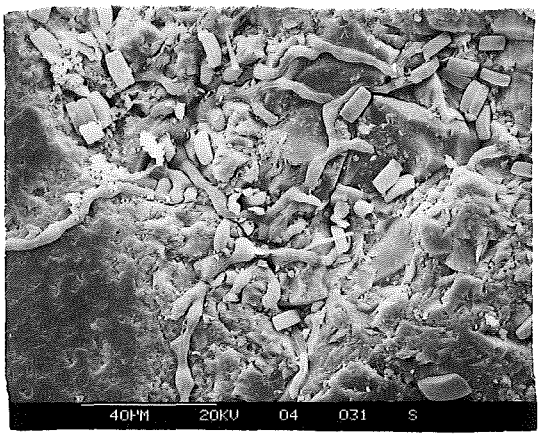
B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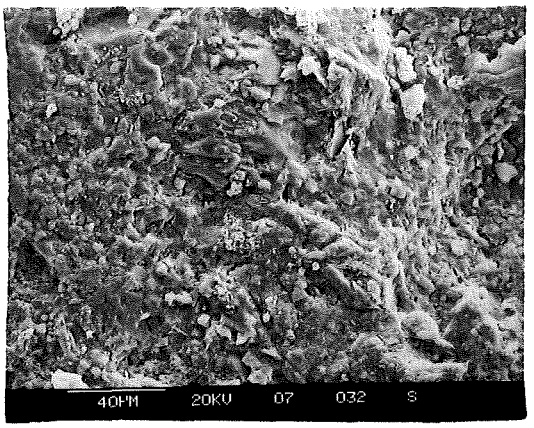
C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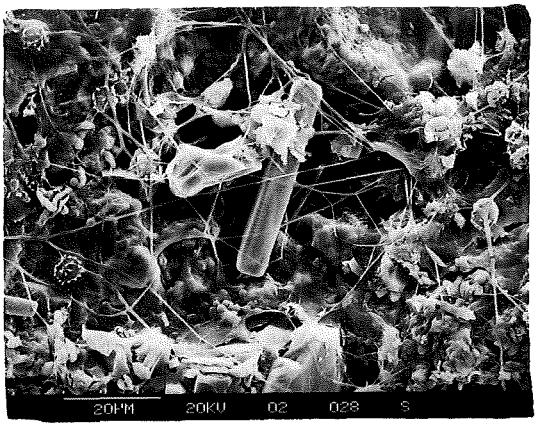
D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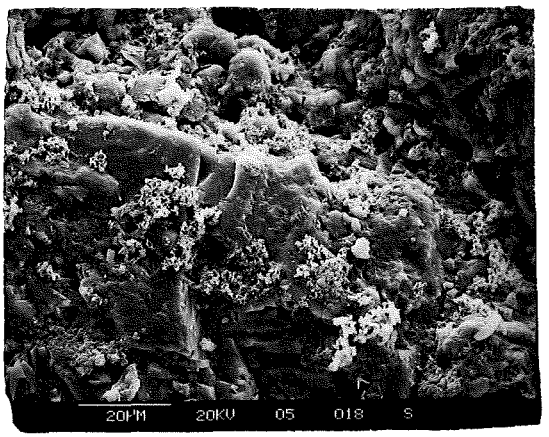
E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F

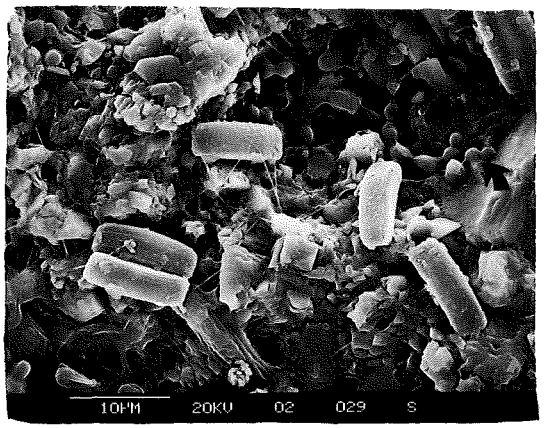
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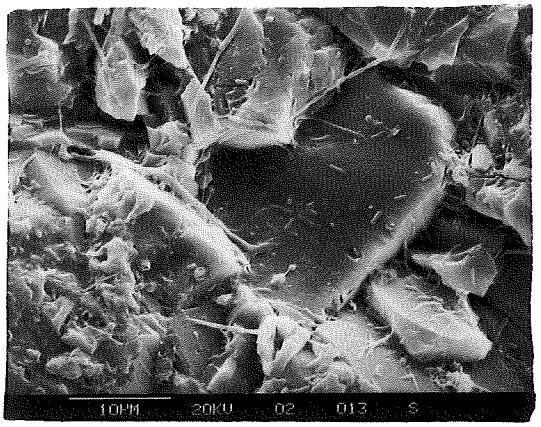
Plate 7.6. Scanning electron micrographs of stone chip surfaces facing downwards at four South Westland sites during May (D & E), September (B) and January (A, C & F). Undersides of stones were colonised predominantly by bacteria and threads (fungi or Actinomycetes). Some filamentous algae were seen in Steep Creek in May (D), but on most other dates amorphous material predominated at this site (e.g., E). Bacteria and threads were common on undersides of stones in Toilet Stream (B & C) and in Suspect Stream in January (F). Some bacteria were also seen on downward facing stone chips in Hidden Creek (A), but were less common there than in Toilet Stream.

A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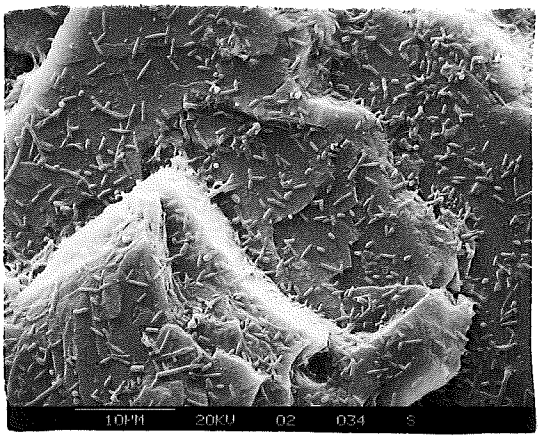
B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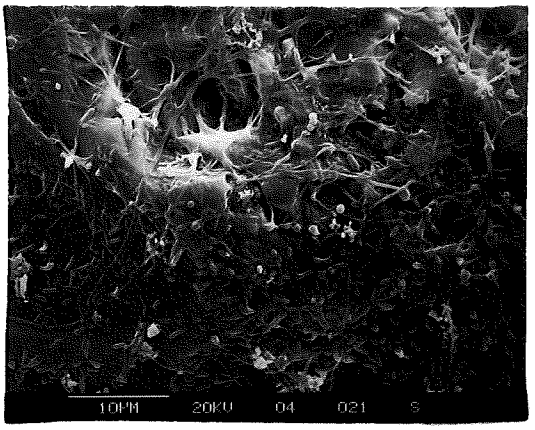
C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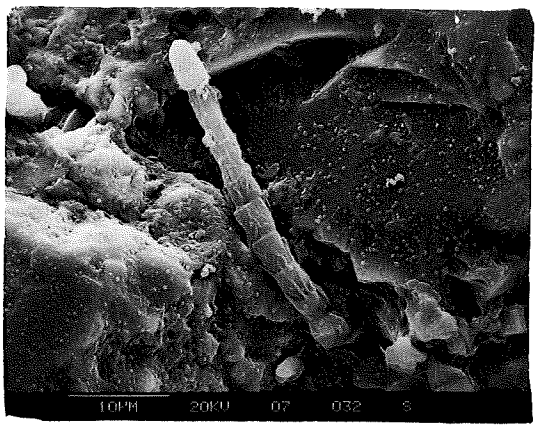
D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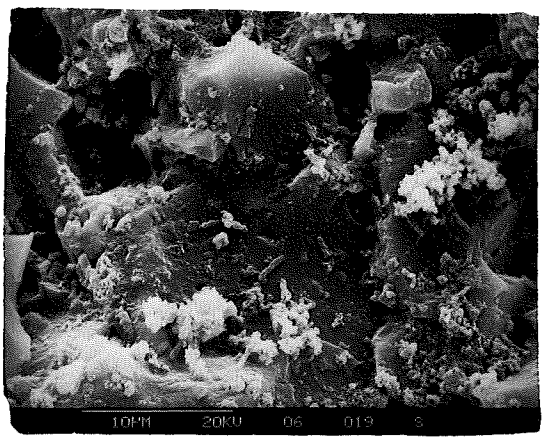
E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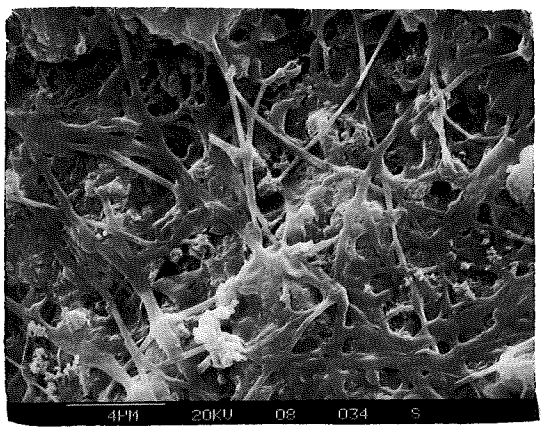
F


4PM 20KV 08 034 S

7.3.2. Elemental Composition

General fields

Eleven elements were identified in epilithon from the four South Westland streams (Fig. 7.1.). Silicon was always the most abundant element because of the presence of diatom frustules and possibly silicate minerals which could have settled out on rod surfaces. In May, silicon counts per second (CPS) were up to 2.7 times higher in Hidden Creek than any at other site, but counts were much higher (up to 3.4 times) in Suspect Stream in November when diatoms appeared to be relatively abundant (see previous section).

Other common elements were potassium and calcium which are both characteristic of organic material, aluminium and iron (Fig. 7.1.). Statistically significant differences between sites (Kruskall-Wallis, $P < 0.05$) were detected on both dates for all major elements (silicon, aluminium, potassium, calcium and iron). Non-parametric multiple range comparisons (Zar, 1974) indicated that epilithon from Hidden Creek and Toilet Stream contained signifcantly ($P < 0.05$) more calcium (4-30 times) than either brownwater site (Table 7.1.). In contrast, Suspect Stream epilithon had significantly higher quantities of iron on both dates, and more aluminium and potassium in November than any other site.

Table 7.1. Between-site, non-parametric multiple range comparisons (Zar, 1974) of EDAX counts for five main elements detected in epilithon on carbon rods removed from four South Westland sites in May and November 1986. Sites are arranged in descending order (i.e., highest counts on the left) with relationships between sites shown as > (significantly different at $P < 0.05$) or = (not significantly different). H, Hidden Creek; T, Toilet Stream; St, Steep Creek; Su, Suspect Stream.

	May	November
Aluminium	Su = T > H > St	Su > H = T = St
Silicon	H > Su > T > St	Su > H = T = Su
Potassium	T = Su = H > St	Su > St > H > T
Calcium	H > T > Su > St	H > T > Su = St
Iron	Su > T > H = St	Su > St = T = H

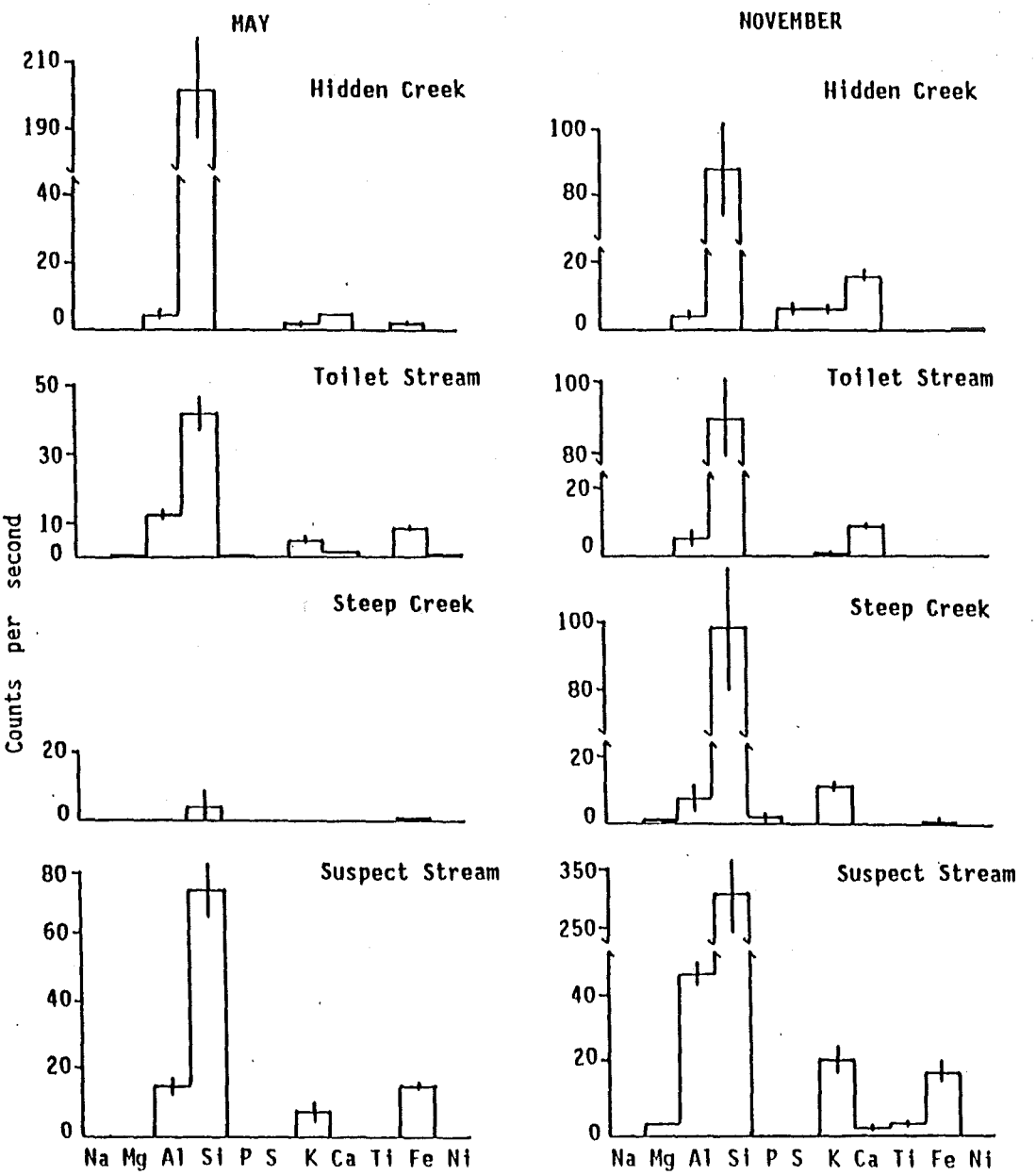


Figure 7.1. EDAX counts ($\bar{x} \pm 1$ SE; n = 5) of X-rays emitted by elements found in epilithon colonising carbon rods incubated in four South Westland streams on two dates.

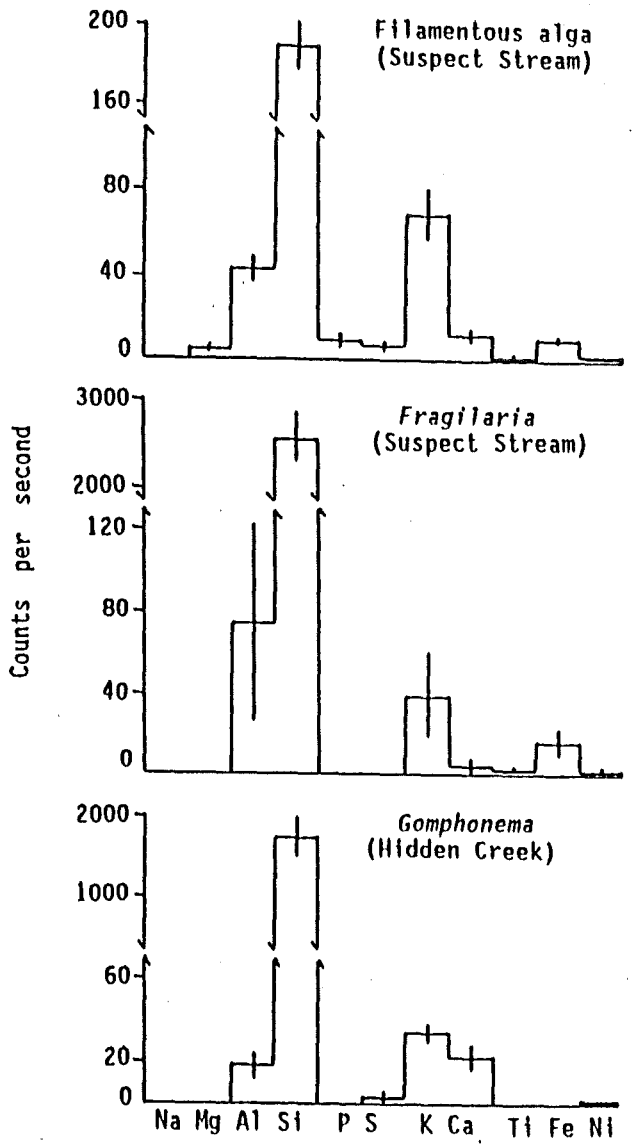


Figure 7.2. EDAX counts ($\bar{x} \pm 1$ SE; n = 5) of X-rays emitted from elements found on diatoms from Hidden Creek (*Gomphonema subclavatum*) and Suspect Stream (*Fragilaria ?vaucheriae*), and algal filaments from the latter site in November 1985.

Diatoms and filamentous algae

Specific components of epilithic communities were analysed to determine the relative abundances of elements that were either adsorbed to, or incorporated into, algal cells. As expected, silicon counts were very high (> 1500 CPS) in frustules of *Gomphonema subclavatum* (Hidden Creek) and *Fragilaria ?vaucheriae* (Suspect Stream) (Fig. 7.2.). Considerable amounts of silicon were also recorded for algal filaments from Suspect Stream, but counts were an order of magnitude lower than for diatoms. Potassium counts were relatively high (35-40 CPS) for both diatom species whereas iron counts were significantly higher for *F. vaucheriae* (Mann-Whitney U, $P < 0.05$). Although mean calcium counts were higher (~5 times) for *G. subclavatum* than *F. ?vaucheriae*, the difference was not statistically significant. Algal filaments contained more potassium than did diatoms from both sites, and also appreciable amounts of iron and aluminium (Fig. 7.2.).

7.3.3. Biomass

Organic carbon

Mean total organic carbon (TOC) concentrations on stones followed seasonal patterns at most sites (Fig. 7.3.). July minima were recorded in Hidden Creek (8.5 $\mu g.cm^{-2}$), Toilet Stream (11.9 $\mu g\ cm^{-2}$) and Suspect Stream (15.0 $\mu g.cm^{-2}$), whereas in Steep Creek, TOC values were low between May and November (21.0-26.3 $\mu g.cm^{-2}$). Summer maxima at any site were recorded in either January 1985 or 1986 and ranged from 21.0 $\mu g.cm^{-2}$ in Toilet Stream to 60.6 $\mu g.cm^{-2}$ in Steep Creek (Fig. 7.3.). Statistically significant differences in stone TOC concentrations between sites (Kruskall-Wallis, $P < 0.05$) were detected in January 1985 and July when concentrations were greatest in Steep Creek.

Photosynthetic pigment

Total pigment concentrations (chlorophyll *a* + pheophytin *a*) measured in September and November 1985 and January 1986 ranged from 0.08 to 0.47 $\mu g.cm^{-2}$, and both extremes were recorded in Hidden Creek (Fig. 7.3.). Mean monthly concentrations at other sites were less variable, particularly in Suspect Stream where they changed by only 0.01 $\mu g.cm^{-2}$ or less between sampling dates. Pigment concentrations were significantly different between sites only in November (Kruskall-Wallis, $P < 0.05$) when concentrations at both clearwater sites were greater than in either brownwater stream.

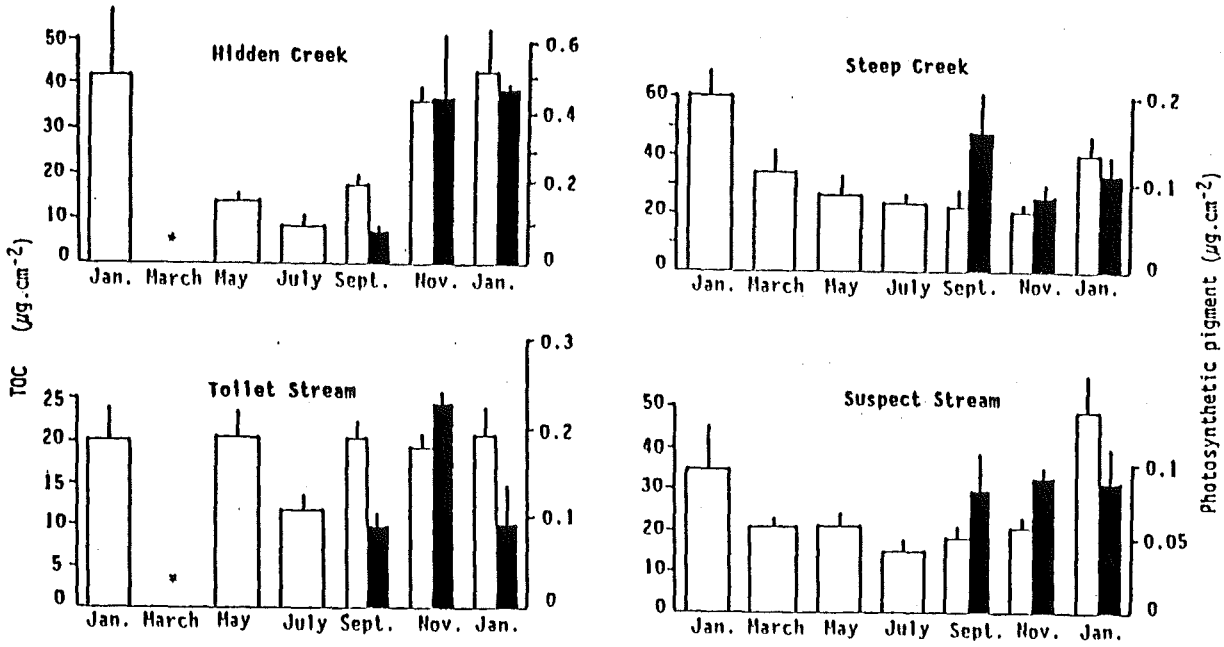


Figure 7.3. Concentrations ($\bar{x}$ + 1 SE; n = 3-6) of total organic carbon (TOC; open bars) and photosynthetic pigment (closed bars) on stones collected from four South Westland streams at bimonthly intervals in 1985-86. Stones collected in January 1985 were taken from the stream bed whereas others were kept in stone trays (see Plate 7.1.). *, analysis failed.

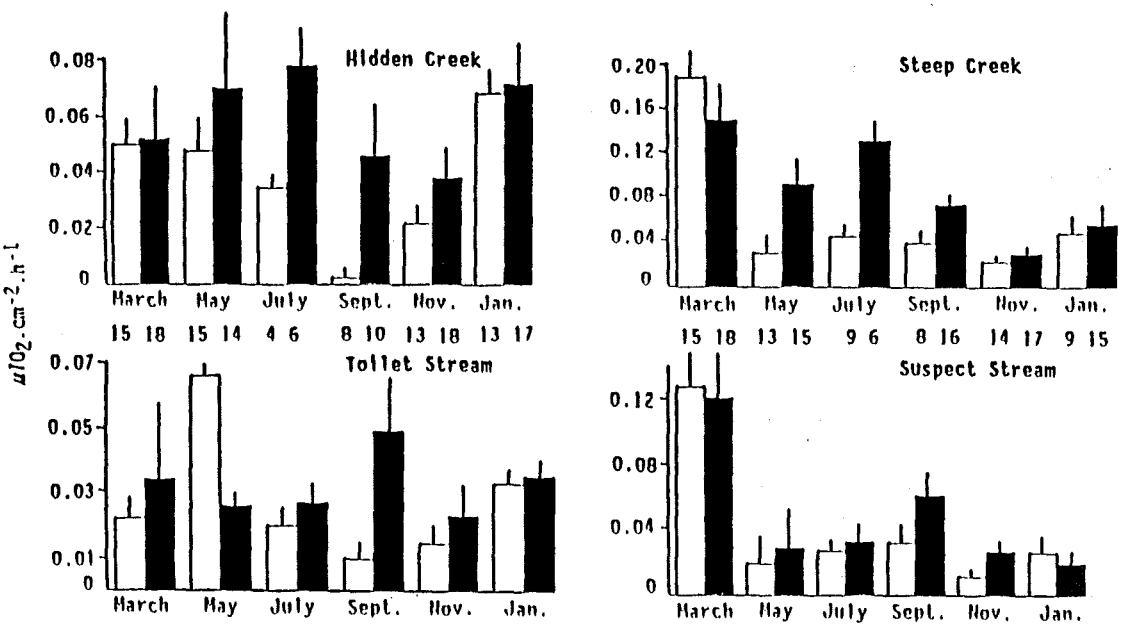


Figure 7.4. Community respiration (open bars) and gross primary production (closed bars) values ($\bar{x}$ + 1 SE; n = 6) for epilithon colonising stones kept in trays in four South Westland streams in 1985-86. Incubation temperatures are given between upper and lower histograms for each pair of simultaneous incubations (Hidden and Toilet or Steep and Suspect). Stream temperatures at the time of collection are given as spot temperatures in Table 4.6.

Pheophytin *a* is a breakdown product of chlorophyll *a* and thus the proportion of chlorophyll in total pigment (chlorophyll + pheophytin) extracts indicates the proportion of healthy algal cells present. On average, chlorophyll *a* comprised 72, 68, 62 and 59 % of total pigment on stones from Hidden Creek, Toilet Stream, Steep Creek and Suspect Stream, respectively, suggesting that a greater proportion (~10 %) of algae in periphyton at the clearwater sites was growing actively.

7.3.4. Respiration and Primary Production

Experimental procedure

Amounts of oxygen consumed or produced by epilithon were very low (< 0.2 $\mu l.cm^{-2}.h^{-1}$) and concentrations in respirometers often approached the detection limit of the oxygen meter (0.1 ppm). In addition, it was difficult to regulate respirometer temperature at the field base, and dark incubations usually were run in slightly colder conditions than light incubations. The greatest discrepancy in incubation temperatures was in September when respiration on stones from Steep Creek and Suspect Stream was measured at 8°C (the same as ambient stream temperature; Table 4.6.), and primary production at 16°C. However, temperatures for equivalent light and dark incubations at the clearwater sites differed by only 2°C in September and all were within 5°C. Because of the low sensitivity of the technique used and variations in incubation temperatures, rates of respiration and primary production by epilithon presented here must be treated with caution.

Community respiration

Amounts of oxygen consumed in the dark by epilithon (community respiration) at temperatures between 4 and 15°C ranged from < 0.01 to 0.19 $\mu l.cm^{-2}.h^{-1}$ (Fig. 7.4.). Highest rates were recorded in March at the brownwater sites and lowest rates were for the clearwater streams in September. Respiration was similar on all dates after March at both brownwater sites (0.01-0.05 $\mu l.cm^{-2}.h^{-1}$). Seasonal changes in respiration rate could be discerned in Hidden Creek and Toilet Stream, but it was not always possible to distinguish these from the effects of changing incubation temperatures. Respiration rates were always greater (1.2-1.8 times) in Steep Creek than Suspect Stream whereas Hidden Creek rates exceeded those in Toilet Stream on four of the six dates.

Primary production

The amount of oxygen produced in light incubations was added to that consumed during dark incubations to give an estimate of gross primary production (Fig. 7.4.). Rates were highest in March in Steep Creek (0.15 $\mu l.cm^{-2}.h^{-1}$) and lowest in November at all sites (0.02-0.04 $\mu l.cm^{-2}.h^{-1}$). Estimates of gross primary production were higher in Hidden Creek than Toilet Stream in all months except September, whereas Steep Creek rates were always greater (up to 4 times) than those in Suspect Stream. No seasonal pattern in primary production was evident at any site (Fig. 7.4.).

7.3.5. Epilithon Grazing by *Deleatidium* Larvae

Organic carbon and photosynthetic pigment concentrations

TOC and photosynthetic pigment concentrations on streambed stones collected concurrently with those used for grazing experiments are shown in Table 7.2. Concentrations of both parameters were greater than any recorded between January 1985 and January 1986 (see Section 7.3.3.). Hidden Creek stones had higher pigment concentrations (> 0.79 $\mu g.cm^{-2}$) but less organic carbon (~80 $\mu g.cm^{-2}$) than stones from Steep Creek (< 0.43 and > 100 $\mu g.cm^{-2}$, respectively). Pheophytin *a* was the dominant photosynthetic pigment on Steep Creek stones on both dates, and in November it comprised 82 % of total pigment. In contrast, chlorophyll *a* was the more abundant pigment on Hidden Creek stones on both dates (75-85 % of total pigment).

Table 7.2. Total organic carbon (TOC), chlorophyll *a* and pheophytin *a* concentrations ($\bar{x} \pm 1$ SE) on stones collected from Hidden Creek and Steep Creek in November 1986 and May 1987. Units are $\mu g.cm^{-2}$; n = 4-6 except for Hidden Creek in May when n = 1.

	November		May	
	Hidden	Steep	Hidden	Steep
TOC	81.8 ±3.6	137.8 ±23.2	78.8 ±21.2	102.4 ±8.9
Chlorophyll a	0.818 ±0.135	0.077 ±0.016	0.675	0.135 ±0.032
Pheophytin a	0.270 ±0.056	0.346 ±0.098	0.123	0.157 ±0.034

Grazing rates

Deleatidium larvae from Steep Creek and Hidden Creek were allowed to feed on stones from each site to determine the quantity and composition (organic and inorganic) of material grazed. Few larvae died during the experiments (1 or 2 larvae in < 20 % of the tubs) and unfed larvae from both sites (May only) produced the same amount of faeces (mean ~137 $mg.g^{-1}.d^{-1}$). Total dry weights of material removed from stones averaged between 146 and 2456 $mg.g^{-1}.d^{-1}$ at 12-16°C, and most of this (61-93 %) was inorganic (Fig. 7.5.). Amounts of organic or inorganic material grazed from stones were similar in both trials (November and May) for each combination of larvae and stones even though epilithon biomass was greater in November. However, there was considerable within-replicate variation for some larva/stone combinations (range of CVs = 28-125 %), although this was less apparent in the second than the first trial (mean CVs = 58 and 76 %, respectively).

Removal rates of organic and inorganic material for all combinations of stones and larvae followed the same rank order on both dates: Steep Creek stones and larvae > Steep Creek stones and Hidden Creek larvae > Hidden Creek stones and Steep Creek larvae > Hidden Creek stones and larvae (Fig. 7.5.). Significant differences in amounts grazed in different combinations were detected for organic and inorganic material on both dates (ANOVA, $P < 0.05$; $\log_e (x)$ or square root (x) transformed). Total amounts (organic + inorganic) of epilithon grazed from Steep Creek stones by all larvae were 2.2 to 16.8 times higher than from Hidden Creek stones and contained proportionately more inorganics (87-93 %) than material grazed from the latter (61-83 %).

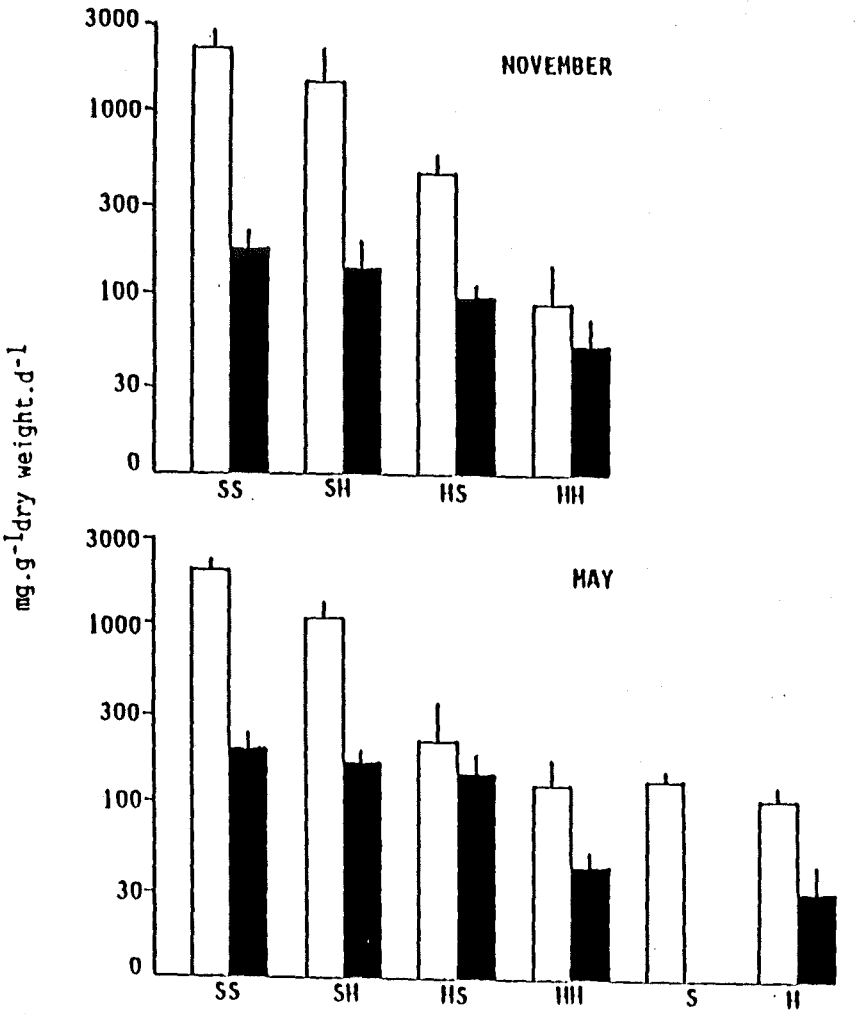


Figure 7.5. Grazing rates ($\bar{x}$ + 1 SE; n = 5) calculated for *Deleatidium* larvae kept with stones from Hidden Creek and Steep Creek in November 1986 and May 1987. Open bars, inorganic material; closed bars, organic material. SS, Steep stones and larvae; SH, Steep stones and Hidden larvae; HS, Hidden stones and Steep larvae; HH, Hidden stones and larvae; S, Steep larvae only; H, Hidden larvae only.

7.4. DISCUSSION

The composition of epilithic algal communities was very different in the two types of streams with diatoms and blue-green algae common at the circumneutral clearwater sites and different species of diatoms and filamentous algae predominating on stones in the acid brownwater streams. Low pH is believed to affect photosynthetic activity and mobility of blue-green algae, and to slow down the division rate of many diatoms (Patrick *et al.*, 1968; Brock, 1973; Patrick, 1977; Tease & Coler, 1984). Nevertheless, some diatoms do live successfully at low pH and several species of *Eunotia* and *Fragilaria* are typical of acid waters in general (Patrick, 1977), and filamentous green algae such as *Stigeoclonium* are characteristic of waters with high metal concentrations (Stokes, 1983). These genera were characteristic colonists of stones at the South Westland brownwater sites whereas *Cocconeis*, *Achnanthes* and *Gomphonema* which were abundant in the clearwater streams are typical colonists of many alkaline, calcium-rich waters (Hynes, 1970; Patrick, 1977).

In general, algal biomass was greater on stones at clearwater than brownwater sites with similar degrees of streambed shading. Artificial channel experiments at Steep Creek (see Appendix VI) suggested that low pH was not restricting algal biomass at the brownwater sites, and indicated that other factors such as reduced light intensity or low nutrient levels may have been limiting. Darkly-stained, humic waters are known to attenuate photosynthetically available radiation (Otto & Svensson, 1983; Towns, 1985; Bowling *et al.*, 1986), but sampling reaches probably were not deep enough for this to affect biomass of algae. However, in short-term experiments, Winterbourn *et al.* (in press and unpublished) found that epilithic algal biomass was nitrogen limited in South Westland brownwater streams, whereas phosphorus was limiting in nearby clearwater streams.

Although algal biomass tended to be higher in the clearwater streams, organic carbon concentrations were generally greater on stones at the brownwater sites. Consequently, organic carbon:chlorophyll ratios (for September and November 1985, January 1986) averaged 322 and 508 in Steep Creek and Suspect Stream, but were much lower in Hidden Creek (126) and Toilet Stream (199). Pheophytin concentrations indicated that biomass of dead algae was slightly higher (by about 10 %) in brownwater streams and would have made a small contribution to the higher carbon:chlorophyll ratios there.

Another important source of organic carbon on stones at the brownwater sites is DOC which can be incorporated into epilithon by abiotic processes (precipitation and adsorption) or by microbial uptake (Lush & Hynes, 1973; Lock & Hynes, 1976; Dahm, 1981; Rounick & Winterbourn, 1983a). Most work in circumneutral stream water has implicated microbial uptake as the dominant mechanism, but Weber *et al.* (1983) observed large increases in the adsorption capacity of humic acid (an important component of DOC) as pH was lowered from 9.0 to 3.5. They concluded that more humic acid functional groups are in an uncharged state at low pH and hence become more adsorbable. Stones collected from brownwater streams in South Westland are typically stained brown, but this colouring disappears following chromic acid digestion indicating that the colouring material is organic. Dickson (1978) found that humic substances precipitated out of brown lake water at pH 4-5 after addition of aluminium, and the precipitation of DOC as metallo-organic complexes may explain the greater abundance of amorphous material seen on stones in Steep Creek and Suspect Stream as well as other brownwater sites in the region (A.K. Graesser, Zoology Dept., University of Canterbury; pers. comm.). Winterbourn *et al.* (1985) also observed a "rather structureless film or amorphous flocculent material" on stones buried in beds of acid streams in Ashdown Forest, southern England, and suggested that abiotic processes dominated DOC uptake on to stone surfaces at these sites.

Given the different composition and structure of epilithon in brownwater and clearwater streams, it seemed likely that this would affect its grazability and nutritive value to invertebrates feeding on stone surfaces. In fact, the amounts of material grazed from Hidden Creek stones (146-574 $mg.g^{-1}.d^{-1}$) were slightly higher than the algal biomass estimated to be removed by *Deleatidium* larvae from stones taken from three circumneutral clearwater streams in the Cass region, mid Canterbury, (26-129 $mg.g^{-1}.d^{-1}$) (Rounick & Winterbourn, 1983a). However, grazing rates on Steep Creek stones were an order of magnitude higher than this (1254-2456 $mg.g^{-1}.d^{-1}$), although still much lower than those obtained by Winterbourn *et al.* (1985) for *Baetis* larvae kept with stones from an acid stream (pH 4.3) in Ashdown Forest (9000 $mg.g^{-1}.d^{-1}$). Epilithic layers from that stream consisted predominantly of an adsorbed organic film with few cellular components, whereas in other Ashdown Forest streams where organic layers were dominated by diatoms and filamentous algae, grazing rates were lower. Similarly, grazing rates were higher for stones from the South Westland brownwater stream where algal biomass was lower, and grazed material

contained proportionately more inorganic material than for stones from the clearwater stream.

Cummins & Klug (1979) suggested that fine-particle feeders can increase consumption rates to compensate for poor food quality. High removal rates of epilithon from Steep Creek stones by *Deleatidium* larvae may be in response to more inorganic material on stones and the apparently large proportion of non-cellular (adsorbed or precipitated) organic carbon which is almost certainly of low nutritive value. Thus, poor food quality could have been a factor limiting densities of fine-particle feeders such as *Deleatidium* in brownwater streams in South Westland. Studies on annual growth rates and assimilation efficiencies are needed to better understand the effects of food quality on benthic invertebrates, but were outside the scope of the present study.

CHAPTER 8

PROCESSING OF KAMAHI LEAVES IN SOUTH

WESTLAND STREAMS

8.1 INTRODUCTION

Allochthonous organic matter represents a substantial proportion (as much as 99 %) of the energy input to forested, headwater streams (Fisher & Likens, 1973; Cummins, 1974). After initial leaching of soluble compounds, leaf breakdown is effected by abiotic fragmentation, microbial decomposition and invertebrate feeding (Kaushik & Hynes, 1971; Petersen & Cummins, 1974; Boling *et al.*, 1975). Conditioning of leaves by bacteria and fungi has been shown to increase the nutritive value of allochthonous leaf litter to detritivores, and some workers have demonstrated selective feeding by invertebrates on suitably colonised leaf material (Anderson & Cummins, 1979; Suberkropp *et al.*, 1983; Arsuffi & Suberkropp, 1984). The recent acidification of many Northern Hemisphere surface waters by acid rain has focussed attention on the effects of low pH on leaf litter breakdown, and several studies have shown that it decomposes more slowly in acidic waters (e.g., Hildrew *et al.*, 1984b; Allard & Moreau, 1986; Mulholland *et al.*, 1987). Some workers have postulated that this can lead to extended temporal availability of autumnal leaf inputs for shredder populations in Northern Hemisphere acid streams (Otto & Svensson, 1983; Mackay & Kersey, 1985).

To determine whether low pH has similar effects on the breakdown of kamahi (*Weinmannia racemosa*: Cunoniaceae) leaf litter in naturally acid streams, I carried out leaf bag studies at two acid brownwater sites (Suspect Stream and Steep Creek) and two circumneutral clearwater sites (Toilet Stream and Hidden Creek) in South Westland (see Fig. 2.3.). I compared weight losses, microbial activity, and invertebrate colonisation of leaves at the four sites and, in an expanded study, used leaf bags of different mesh sizes to investigate the relative contributions of microbial and invertebrate processing to leaf litter breakdown. In addition, I conducted feeding trials with larvae of a large-particle detritivore and kamahi leaves conditioned in brownwater and clearwater streams.

8.2. PRELIMINARY STUDY

8.2.1. Methods

Leaf bags

Kamahi leaves were collected from a single tree near Okarito in January 1985 and returned to the laboratory where 15 g (± 0.005 g) of fresh leaf material were placed in each of fifty-three 1 mm mesh bags (15 x 12 cm). All bags were heat-sealed and dried for seven days at 50°C. Dry kamahi leaves are very brittle, and therefore the contents of only five leaf bags were reweighed to estimate the initial dry weight of leaves (fresh weight x 0.47). On 25-27 March 1985, twelve bags were immersed in each of Hidden Creek, Toilet Stream, Steep Creek and Suspect Stream in commercial grade onion sacks which were anchored with heavy rocks and secured by rope to adjacent trees.

Bags were removed from the streams in sets of three on 9 May, 22 August, 27 November 1985 and 28 January 1986 (i.e., after 42, 148, 244 and 306 days incubation, respectively). All bags were frozen within three hours of collection except in August and September when one bag from each set was kept cool in stream water until microbial respiration rates could be measured (starting eight hours later). In the laboratory, frozen leaves were thawed, washed over a 0.25 mm mesh net to collect invertebrates, dried and weighed. Invertebrates were identified and counted under a binocular microscope.

Microbial respiration

Leaves used to measure microbial respiration were rinsed gently to remove invertebrates and 0.313-0.990 g (final dry weight) of leaf material was placed in glass respirometers (volume 110 m*l*, n = 5 per site) containing water (9°C) from the same stream in which the leaves had been held. Experimental and blank respirometers containing water only were sealed with rubber bungs, ensuring that no air was trapped inside, and incubated in the dark at 9°C for 9-11 hours. After incubation, oxygen consumption was measured with a YSI Model 54 meter and adjusted for respirometer volume. Leaves were frozen and later dried and weighed so that oxygen consumed could be expressed per gram of leaf dry weight.

Scanning electron microscopy

Leaves removed from the four streams after 148 days were examined by scanning electron microscopy (SEM) to enable a qualitative assessment of microbial colonisation and leaf surface breakdown to be made. Sections (~1 cm^2) of leaf were excised immediately after removal from bags and placed in 3 % gluteraldehyde in phosphate buffer. Later, they were rinsed twice in phosphate buffer, dehydrated in an alcohol series (Rounick & Winterbourn, 1983a), air-dried and mounted on SEM stubs with double-sided cellotape. After coating with 50 nm of carbon/gold palladium, leaf surfaces were viewed with a Cambridge Stereoscan MK II SEM at magnifications up to 5000 times.

8.2.2. Results

Leaf breakdown

By the end of the experiment (306 days), leaves in both clearwater streams had become severely fragmented and only the skeletal framework of many remained. Evidence of invertebrate feeding on leaf margins was seen after 148 days (August) in Hidden Creek and, to a lesser degree, in Toilet Stream. In contrast, very little evidence of feeding or skeletonisation of leaves incubated in the brownwater streams was apparent and only slight fragmentation had occurred after 306 days.

Weight losses assessed on day 42 were similar at all sites (24.6-31.7 % dry weight), but subsequently, leaf breakdown followed the sequence Hidden Creek > Toilet Stream > Steep Creek > Suspect Stream (Fig. 8.1.). By the end of the experiment, only 25 % of initial leaf biomass remained in bags from Hidden Creek compared with 60 % in bags from Suspect Stream. Statistically significant differences (ANOVA, $P < 0.05$; $\log_e (x)$ transformed) in dry weights of leaf material remaining were found between Hidden Creek and all other sites on days 148 and 244, and between pairs of clearwater and brownwater streams on day 306.

Decay coefficients (-k) for leaves were calculated using the exponential decay model of Petersen & Cummins (1974) which is expressed by the formula: $\log_e(\%R/100)/t$, where R is the amount of leaf material remaining after t days in the stream. Petersen & Cummins (1974) calculated -k using a least squares fit of the data assuming an asymptote of zero, but this procedure may not be appropriate if rapid initial weight loss is followed by a slow decline in leaf biomass, as in Steep Creek and Suspect Stream.

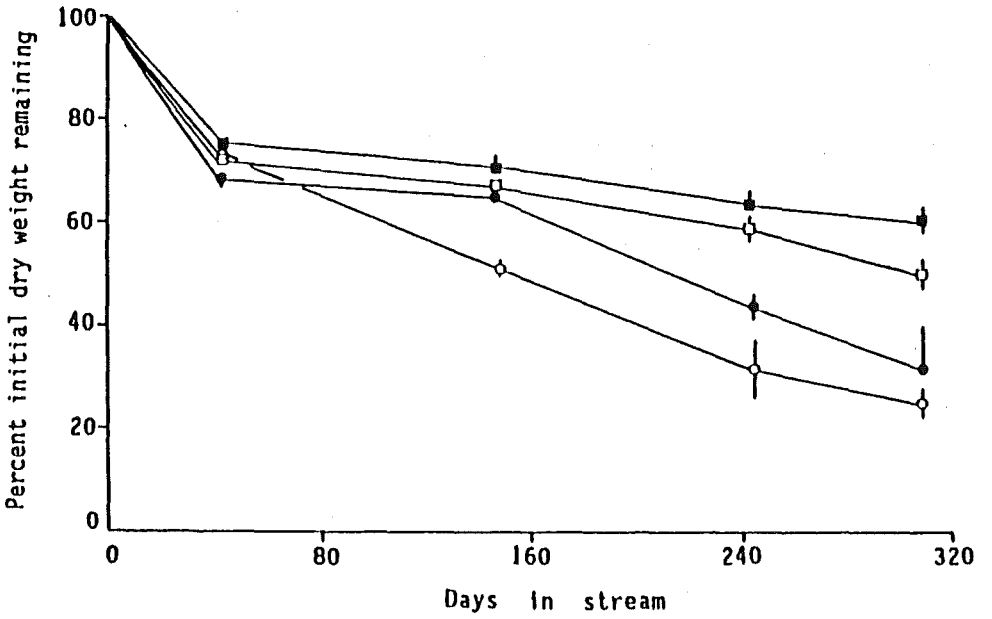


Figure 8.1. Percent initial dry weight of leaves remaining ($\bar{x} \pm 1$ SE, n = 3) in 1 mm mesh bags held in Hidden Creek (○), Toilet Stream (●), Steep Creek (□) and Suspect Stream (■) between March 1985 and February 1986. Error bars are not shown if accomodated within the symbol.

Table 8.1. Decay coefficients (-k) and half-lives (t_{50}) of leaves held in 1 mm mesh bags in four South Westland streams in 1985-86. Decay coefficients and half-lives were calculated from the least squares fit of data including (no parentheses) and excluding (parentheses) day 0.

	-k	t_{50} (days)
Hidden Creek	0.0039 (0.0043)	176 (163)
Toilet Stream	0.0034 (0.0035)	203 (198)
Steep Creek	0.0026 (0.0022)	270 (321)
Suspect Stream	0.0022 (0.0014)	321 (480)

Therefore, I calculated -k values and half-lives of leaves with and without day 0 included in the data set (Table 8.1.). The -k values for leaves from clearwater streams were 1.3-1.8 times greater than for leaves from brownwater streams and the differences between the two sets were even greater (1.6-3.1 times) when day 0 was excluded from the calculations. Thus, the calculated half-life of leaves from Suspect Stream was 159 days longer when day 0 was excluded (Table 8.1.).

Microbial respiration and electron microscopy

Oxygen uptake by microbial communities on leaves removed from the streams in August and November 1985 ranged from 24.8 to 73.4 $\mu l.g^{-1}.h^{-1}$ and was higher at all sites in November (Fig. 8.2.). No significant differences (ANOVA, $P > 0.05$; $\log_e (x)$ transformed) in respiration rates were detected between sites at this time, but in August rates were significantly higher for Hidden Creek and lower for Steep Creek than for any other site (Duncan's New Multiple Range test, $P < 0.05$).

SEM examination of leaf surfaces after 148 days incubation (August) showed that fungi were the main microbial colonists of leaves at the brownwater sites whereas bacteria tended to be more common at the clearwater sites (Plate 8.1.). However, fungi were not always associated with leaf surfaces and often were interwoven with amorphous material which tended to accumulate on leaves at the brownwater sites (Plate 8.1C.). Surfaces of leaves from the clearwater streams were comparatively free of amorphous material, and upper tissue layers had been removed in places (Plate 8.1A.).

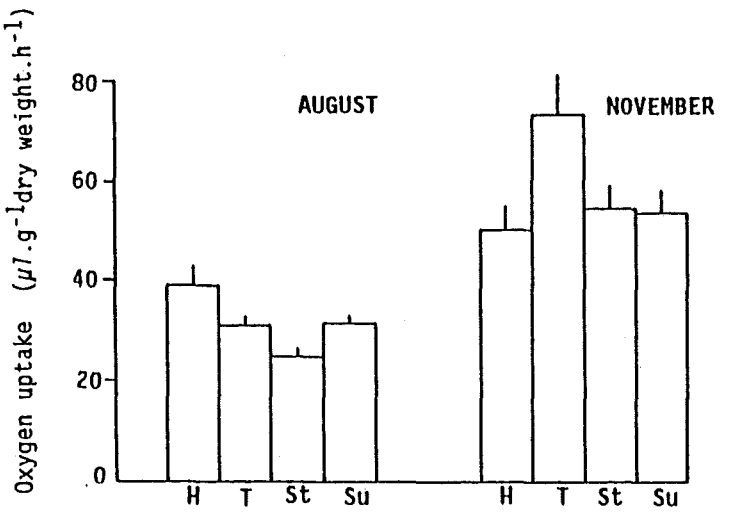


Figure 8.2. Respiration rates ($\bar{x}$ + 1 SE, n = 5) of microbial communities associated with leaves removed from four South Westland streams in August and November 1985 (after 148 and 244 days in the streams, respectively). H, Hidden Creek; T, Toilet Stream; St, Steep Creek; Su, Suspect Stream.

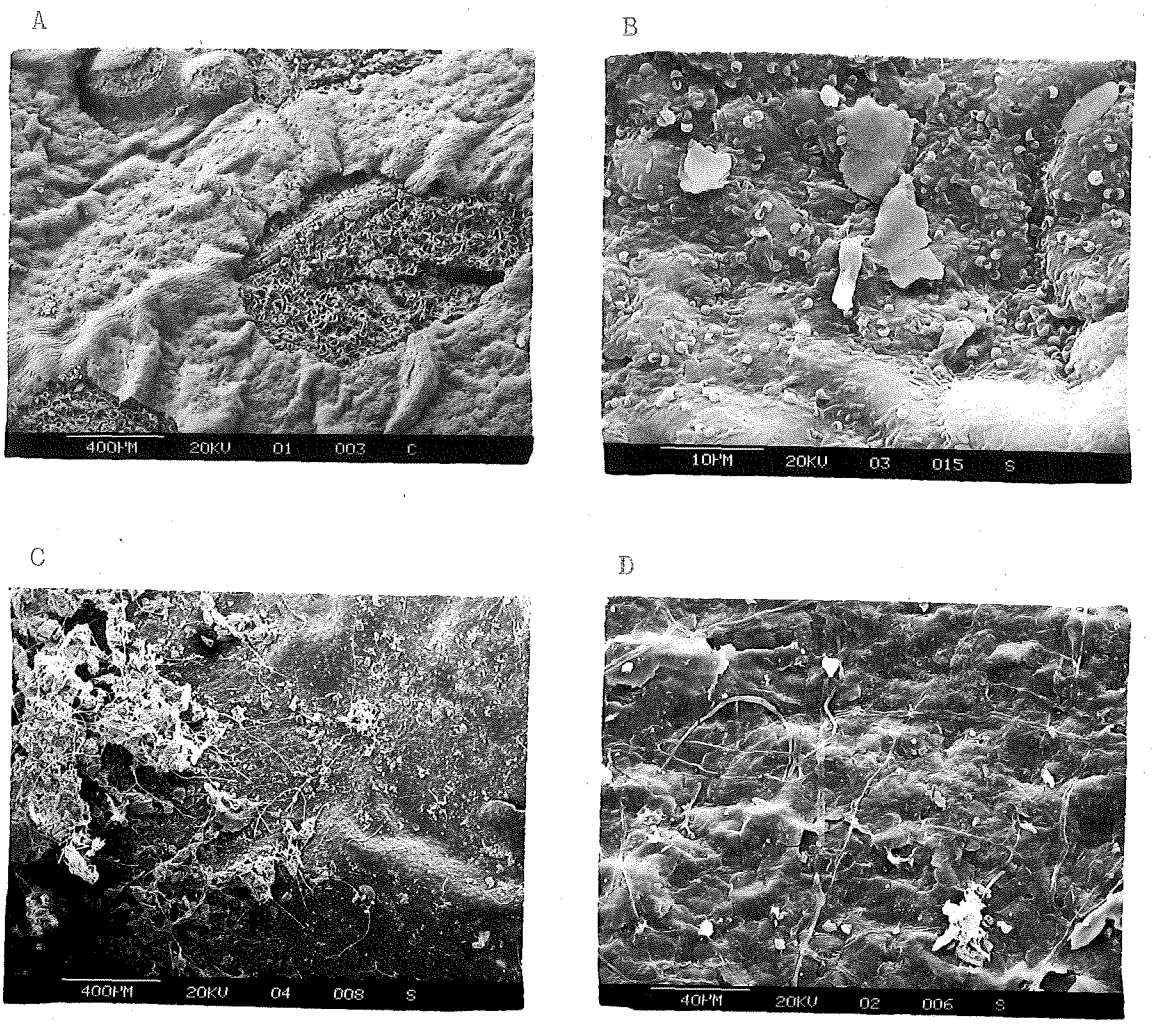


Plate 8.1. Scanning electron micrographs of kamahi leaf surfaces after 148 days (March-August 1985) in 1 mm mesh bags in Hidden Creek (A), Toilet Stream (B) and Steep Creek (C and D). Fungi were the dominant microbial colonists on leaves at the brownwater sites (e.g., Steep Creek) but these often were associated with amorphous material on the leaf surface (C). In contrast, leaves from the clearwater sites (Hidden Creek and Toilet Stream) were relatively clean and upper tissue layers had been removed in places (A). Bacteria appeared to be the most common microbes on leaves at these sites (B).

Colonisation by invertebrates

Thirty invertebrate taxa were taken from bags kept at the four sites (Table 8.2.). Most (20) occurred in bags held in Toilet Stream and least (8) were found in Suspect Stream. Chironomids were common at all sites, and in the brownwater streams they accounted for about 90 % of the total bag fauna. In contrast, the hydrobiid snail, *Potamopyrgus antipodarum*, was by far the most common colonist in Toilet Stream bags whereas the stonefly *Austroperla cyrene* shared dominance with chironomids in Hidden Creek bags. Larvae of *A. cyrene* and *Olinga feredayi*, the commonest caddisfly in bags from Hidden Creek, are known to eat decomposing leaves (Winterbourn, 1982), whereas *Triplectides* sp., the most abundant trichopteran in Toilet Stream bags is an obligate shredder of leaves and wood. Gut content analysis showed that *Oeconesus* sp., which was found in small numbers in bags in Toilet Stream, also can consume coarse particulate organic matter.

Table 8.2. Percentage composition of the invertebrate faunas colonising 1 mm mesh leaf bags removed from four streams in August and November 1985 and January 1986 (all bags combined).

	Clearwater		Brownwater	
	Hidden	Toilet	Steep	Suspect
ANNELIDA				
OLIGOCHAETA	10.7	5.0	0.9	4.3
MOLLUSCA				
GASTROPODA				
Potamopyrgus antipodarum	0	50.6	0	0
ARTHROPODA				
ARACHNIDA				
ACARINA	1.1	0.3	0.4	0.5
CRUSTACEA				
AMPHIPODA	0	0.9	0	1.1
OSTRACODA	1.1	0.3	0.4	0.5
INSECTA				
EPHEMEROPTERA				
Deleatidium spp.*	3.4	6.3	1.3	0
Mauiulus luma	0.4	0.3	0	0
Ameletopsis perscitus	0	0	0.2	0
PLECOPTERA				
Austroperla cyrene	30.3	1.3	0.6	0
Cristaperla fimbria	1.1	0	0	0
Spaniocerca longicauda	1.9	7.5	0	0
Stenoperla maclellani	3.4	0.9	0	0
Zelandobius confusus	0	0	0.8	0
TRICHOPTERA				
Olinga feredayi	8.0	0.6	0	0
Oconesus sp.	0	0.6	0	0
Philorheithrus agilis	3.1	1.3	0	0
Triplectides sp.	0	5.7	0	0
Rakiura vernale	0	0	0.2	0
Zelolessica cheira	0	0	0.2	0
Hydrobiosis sp.	0.4	0	0	0
Psilochorema sp.	0	0	0	0.5
Hydrobiosidae indet.	0.8	0	0	0
Polyplectropus sp.	0	0	0.4	0
DIPTERA				
Chironomidae	33.0	15.1	92.1	88.8
Empididae	1.1	0.3	0	0.5
Eriopterini	0	0.3	0	0
Ceratopogonidae	0	2.2	2.4	3.7
Paralimnophila skusei	0	0.3	0	0
Muscidae	0	0	0.2	0
Total numbers	261	318	533	188

*, Two subgroups (*lillii* and *myzobranchia*) were assumed to be present at the clearwater sites, but only the *lillii* subgroup was at the brownwater sites (see Section 6.3.1.).

8.3. BRIDGING SECTION

Most of the initial rapid loss in leaf weight (~28 %) observed on day 42 in all streams is assumed to be attributable to leaching of soluble compounds in the first few days of the experiment (Kaushik & Hynes, 1971; McCammon, 1980). Because leaf-shredding invertebrates were absent from bags in Suspect Stream and constituted only a minor proportion (0.6 %) of the fauna in bags in Steep Creek, post-leaching weight losses at these sites can be attributed primarily to microbial decomposition. However, large-particle detritivores made up about 38 and 8 % of the numbers of animals in bags from Hidden Creek and Toilet Stream, respectively, indicating that post-leaching weight losses at these sites were the result of microbial breakdown and invertebrate feeding.

A problem with the use of 1 mm mesh bags in the present study was that they did not allow all invertebrates free access to and from enclosed leaves. Small insect larvae were able to enter the bags freely, but it seemed that some grew to such a size that they were prevented from leaving, and presumably had no choice but to feed on the leaves. This may have contributed to some of the between-bag variability in leaf weight losses shown in Figure 8.1., although the effect of this on leaf breakdown may have been counterbalanced to some extent by the exclusion of large detritivores from bags.

Several workers have used oxygen uptake as an indicator of decomposition rate (e.g., Petersen & Cummins, 1974; Rounick & Winterbourn, 1983b; Allard & Moreau, 1986). However, my preliminary study suggests that this need not always be valid since some microbes (e.g., the fungi shown in Plate 8.1C.) appeared to use leaf surfaces primarily as a physical substratum and had little or no involvement in leaf breakdown. Thus, oxygen uptake rates of leaves at the brownwater sites almost certainly overestimated decomposer activity.

To investigate the relative importance of microbes and invertebrates in kamahi leaf breakdown, I decided to conduct an expanded study in Hidden Creek and Steep Creek using leaf bags of three mesh sizes:

1) 0.2 mm to exclude macroinvertebrates;
2) 1 mm to enable comparisons with the preliminary study;
3) 7 mm to allow free passage for all invertebrates.

In addition, I used 7 mm mesh bags filled with plastic strips to distinguish between invertebrates feeding on leaves and those using bags

primarily for shelter and/or other sources of food (e.g., fine particulate matter). Because the pool of potential leaf bag colonists was likely to change during the course of the experiment, I used the sampling protocol adopted by Collier & Winterbourn (1986) whereby bags introduced into streams at different times were removed on the same date. Laboratory trials were conducted with larvae of the stonefly *Austroperla cyrene* to assess ingestion rates and palatability of leaves conditioned in Hidden Creek and Toilet Stream.

8.4. EXPANDED STUDY

8.4.1. Methods

Leaf bags

Kamahi leaves were collected from several adjacent trees in North Westland in April 1986 and returned to the laboratory where fresh leaves (5 or 10 g ± 0.005 g) or plastic strips were placed in "bags" of three mesh sizes:

1) 10 g in 7 mm mesh bags (15 x 14 cm);
2) 10 g in 1 mm mesh bags (15 x 12 cm);
3) 5 g in PVC tubes (10 cm long; 4 cm diameter) covered at both ends with 0.2 mm mesh;
4) 10 black polythene strips (3 x 12 cm) in 7 mm mesh bags (15 x 14 cm).

All bags were sealed and those containing leaves were dried for seven days at 50°C. Dried leaves from five bags were reweighed to estimate their initial dry weight (fresh weight x 0.40). Sets of three or four bags were placed in commercial grade onion sacks in Hidden Creek and Steep Creek on 13 May, 26 August and 12 November 1986.

Three other 0.2 and 7 mm mesh bags containing leaves were not placed in the streams but otherwise were treated identically, and were reweighed at the end of the experiment to determine if any leaf biomass losses could be attributed to storage or transport. Mean weight losses were 0.9 % (7 mm mesh) and 0.3 % (0.2 mm mesh) of initial dry weight, indicating that storage and transport losses had negligible effects on final leaf weight.

Bags were removed from both streams on 5-7 January 1987 (i.e., incubation times of 54, 133 and 238 days) and placed in separate plastic bags. Three bags from each set were frozen within three hours of collection and the others were kept cool (5°C) in stream water prior to use in respiration and feeding experiments (see following methods sections). In the laboratory, frozen leaves were thawed, washed over a 0.15 mm mesh net to remove fine debris and invertebrates, dried and weighed. Invertebrates colonising 0.2 mm and 7 mm mesh bags were identified and counted.

Microbial respiration and scanning electron microscopy

Oxygen consumption rates of leaves kept in 0.2 mm mesh bags were measured using the method described in Section 8.2.1. Leaves which had been in the streams for 54, 133 and 238 days were incubated in water from the same stream for 7-9 hours at temperatures ranging from 13 to 20°C (depending on ambient air temperatures). Then a second incubation was carried out in water from the alternate stream (brownwater or clearwater) to determine if microbial respiration rates were affected by the water chemistry.

Sections of leaves held in streams in 0.2 and 7 mm mesh bags for 133 and 238 days and non-incubated leaves were prepared for scanning electron microscopy and examined as described in Section 8.2.1.

Leaf consumption trials

Larvae of the large-particle detritivore, *A. cyrene*, were collected from Hidden Creek in January 1987 and returned to the field base. Unstarved larvae (body length 10-20 mm) were placed in plastic tubs (volume 250 m*l*) containing Hidden Creek water and leaves (*ad libatum*) which had been incubated in 0.2 mm mesh bags in Hidden Creek or Steep Creek for 238 days (9 larvae per tub; 3 tubs per treatment). Controls containing larvae and plastic mesh instead of leaves were run concurrently to determine the amount of faeces produced without feeding.

Larvae were left in the dark for three days (temperature range 13-21°C) after which they were removed, preserved in 10 % formalin and later dried and weighed. Faecal material produced during the experiment was filtered on to ashed, pre-weighed GF/C glass fibre filters with a Millipore apparatus. Filters were dried, weighed, ashed overnight at 500°C and reweighed to estimate amounts (total and inorganic) of material present. The weight of organic material was obtained by difference. Blank filters subjected to all the above procedures were used to make any adjustments that were necessary as a result of changes in filter weight.

Food choice experiment

Some of the *A. cyrene* larvae collected in January 1987 were starved for about 60 hours and used in a food choice experiment conducted in the dark at 18°C. Nine larvae (body length ~10 mm long) were placed in the centre of tubs (250 m*l*; n = 3) filled with Hidden Creek water and offered three sections (4 x 2 cm) of leaf:

1) dried and leached in distilled water for 5 days;
2) incubated in 0.2 mm mesh bags in Hidden Creek for 238 days;
3) incubated in 0.2 mm mesh bags in Steep Creek for 238 days.

Positions of larvae (i.e., "choices") were recorded hourly for three hours.

8.4.2. Results

Leaf weight loss

Leaves lost an average of 28 % (range 22.0-36.3 %; all bags combined) of initial dry weight in the first 54 days of the experiment, but subsequent weight losses varied widely between sites and in bags of different mesh sizes (Fig. 8.3.). In Steep Creek, very little additional leaf weight loss was recorded in any bags during the experiment and 61-71 % of initial leaf biomass remained after 238 days. In contrast, only one 7 mm mesh bag held in Hidden Creek had any leaf material left after 238 days whereas an average of 56 % (range 33-72 %) of initial leaf biomass remained in 0.2 mm mesh bags (Fig. 8.3.). By the end of the experiment, leaves kept in 0.2 mm mesh bags in Hidden Creek were dark brown and soft, but in Steep Creek they were still tough and yellow-green in colour, indicating that comparatively little microbial breakdown had occurred at the latter site.

Decay coefficients (-k) and half-lives were calculated as described in Section 8.2.2. They confirmed that leaves broke down in the sequence 7 mm > 1 mm > 0.2 mm and that breakdown was much faster in Hidden Creek (Table 8.3.). Thus, half-lives of leaves (excluding day 0 from the calculation) in 7 mm mesh bags were 309 days shorter in Hidden Creek than Steep Creek. As noted in the preliminary study, exclusion of day 0 data had a marked effect on calculated breakdown rates of leaves particularly in Steep Creek where half-lives of leaves in 0.2 mm mesh bags differed by 446 days (Table 8.3.). However, in Hidden Creek the effect was not as pronounced, and in 7 mm mesh bags, half-lives actually decreased if day 0 was excluded. Decay coefficients calculated from data

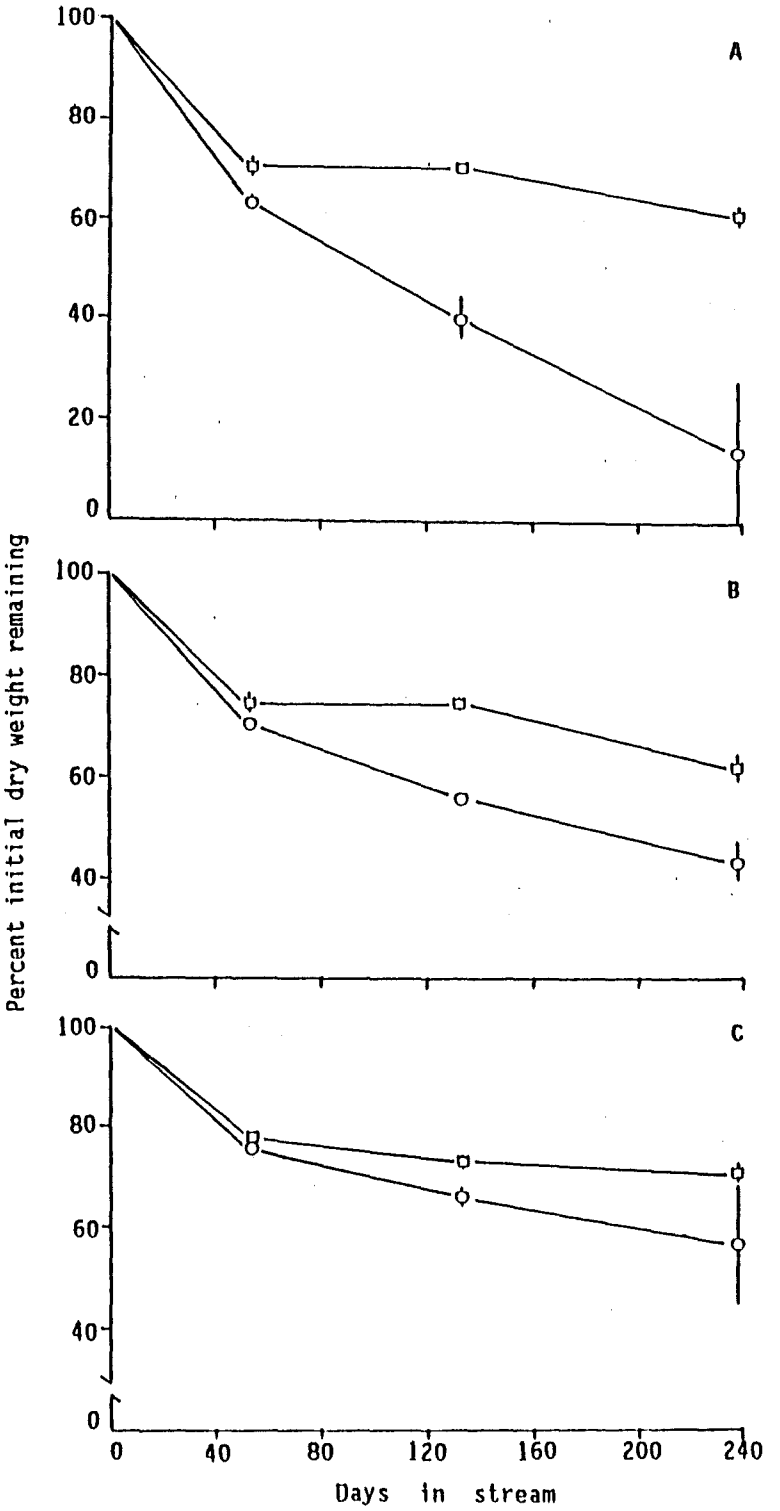


Figure 8.3. Percent initial dry weight of leaves remaining ($\bar{x}$ ± 1 SE, n = 3) in 7 mm (A), 1 mm (B) and 0.2 mm (C) mesh bags kept in Hidden Creek (○) and Steep Creek (□) between May 1986 and January 1987. Error bars are not shown if accomodated within the symbol.

for 1 mm mesh bags (including day 0) were identical to those recorded in Hidden Creek and Steep Creek in the preliminary study (see Table 8.1.).

Table 8.3. Decay coefficients (-k) and half-lives (t_{50}) of leaves held in 0.2, 1 and 7 mm mesh bags at two sites in 1986-87. Decay coefficients and half-lives were calculated from the least squares fit of data including (no parentheses) and excluding (parentheses) day 0.

	-k	t_{50} (days)
Hidden Creek		
0.2	0.0030	232
	(0.0023)	(297)
1	0.0039	176
	(0.0037)	(187)
7	0.0058	119
	(0.0068)	(102)
Steep Creek		
0.2	0.0023	302
	(0.0009)	(748)
1	0.0026	264
	(0.0019)	(367)
7	0.0029	236
	(0.0017)	(411)

Microbial respiration

Oxygen uptake rates recorded for leaves in January 1987 ranged from 60.6 to 128.5 $\mu l.g^{-1}.h^{-1}$ (Fig. 8.4.) and generally were higher than those measured in the preliminary study (see Section 8.2.2.). For leaves from Steep Creek, rates measured in Steep Creek water increased with the time leaves had been in the stream, but for leaves from Hidden Creek, microbial respiration rate was lowest after 238 days, in Hidden Creek water (Fig. 8.4.).

Because incubation temperatures varied, direct comparisons between oxygen uptake rates of the same leaves incubated in different waters (brown or clear) could be made for both sites only on day 54, for Steep Creek leaves on day 133 and for Hidden Creek leaves on day 238 (Fig. 8.4.). The only significant difference (Mann Whitney U-test, $P < 0.05$) in oxygen consumption recorded was on day 54 when rates on leaves from Steep Creek were lower in circumneutral, clear water than in acid, brown water.

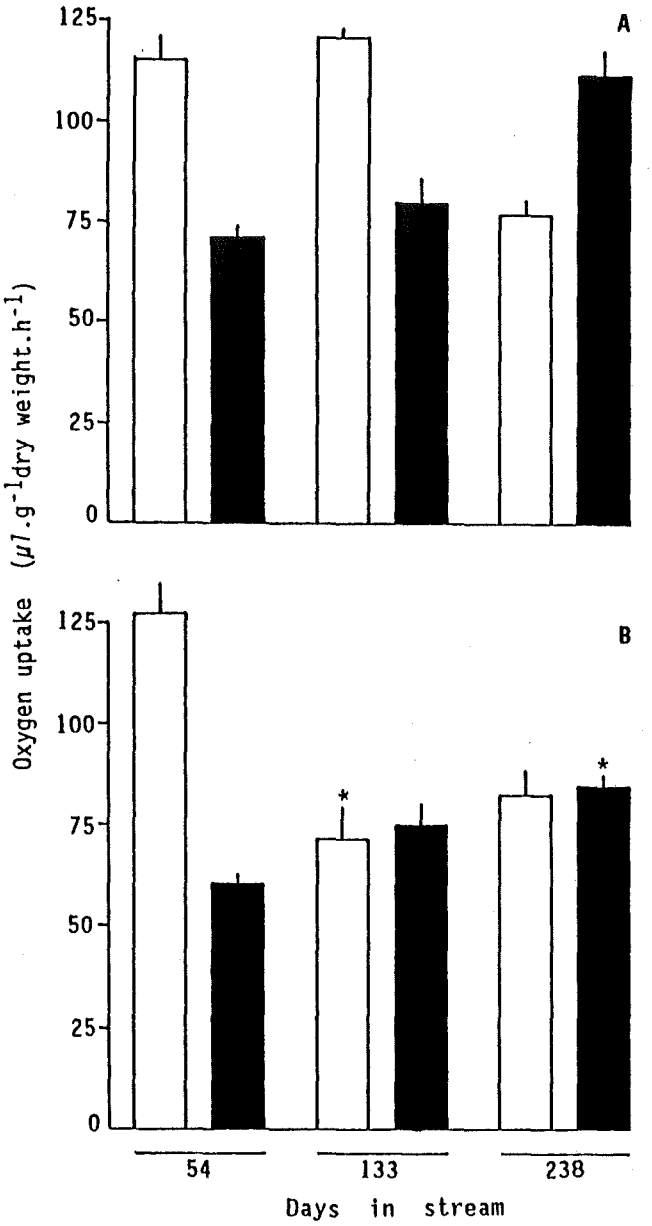


Figure 8.4. Respiration rates ($\bar{x}$ + 1 SE, n = 5) of microbial communities associated with leaves removed from Hidden Creek (open bars) and Steep Creek (closed bars) after 54, 133 and 238 days in 1986-87. A, assays in water from the stream where leaves were conditioned. B, assays in water from the alternate stream. Incubations were conducted at 18 ± 2°C except for two samples (*) where the temperature was 13°C.

Electron microscopy

Scanning electron microscopy of non-incubated leaf surfaces showed that before introduction to the streams, leaves had an intact epidermis which was generally free of foreign material although colonised by some terrestrial fungi (Plate 8.2A.). Few bacteria were seen in high power examinations of their surfaces. In contrast, leaves kept in 7 mm mesh bags in Hidden Creek had lost a substantial proportion of the epidermis by day 133 (Plate 8.2B.). After 238 days in 0.2 mm mesh bags, most of the epidermis had gone completely (Plate 8.2D.) so that internal tissues were exposed to microbial colonisation (Plate 8.2E.). Areas of intact epidermis were colonised mostly by bacteria and narrow filamentous organisms, possibly Actinomycetes (Plates 8.2C. & F.).

Surfaces of leaves from Hidden Creek generally seemed to be free of debris, but in Steep Creek most leaves were covered by a loose matrix of amorphous material (Plate 8.3A. & B.) interwoven with fungal hyphae and containing high densities of spores of the aquatic hyphomycete *Casaresia sphagnorum* (Plate 8.4A. & B.) (R.A. Aimer, Biological Sciences Department, University of Waikato; pers. comm.). Beneath this outer matrix, very high densities of other fungal hyphae (most were probably a *Pythium* species; Plate 8.4D.) ramified over the leaf surface (Plates 8.3D. & E.) and formed a discrete layer which often became detached during washing. Few bacteria were seen on leaves from Steep Creek and, despite dense colonisation by fungi, very little breakdown of the epidermis was evident on either date that leaf surfaces were viewed with the SEM (Plate 8.3C. & F.).

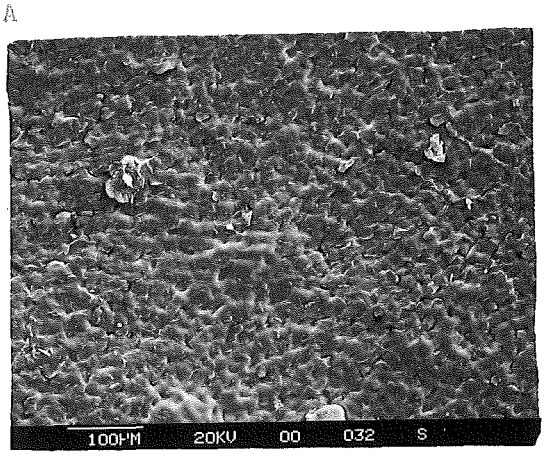
Composition of bag faunas

Chirononmid larvae comprised 75 and 97 % (24-122 larvae in three "bags") of the fauna found in 0.2 mm mesh bags from Hidden Creek and Steep Creek, respectively (Table 8.4.). Few other taxa entered the 0.2 mm mesh bags, although some nematodes, ostracods and larvae of *Spaniocerca longicauda* (Plecoptera) were present in those from Hidden Creek.

Twenty-two invertebrate taxa were taken from 7 mm mesh bags held in Hidden Creek and 17 were found in Steep Creek bags (Table 8.5.). Numbers of taxa colonising bags containing leaves or plastic strips were almost identical at each site (21 and 19 in Hidden Creek, and 15 and 14 in Steep Creek) although relative abundances of taxa differed. Faunas of 7 mm mesh bags in Hidden Creek were dominated by chironomids, nematodes and harpacticoid copepods but only the last-named taxon was represented better in leaf bags than in bags containing plastic strips. Numbers of *A.*

Plate 8.2. Scanning electron micrographs of kamahi leaf surfaces after 0-238 days immersion in Hidden Creek (removed January 1987). Before introduction to the streams, leaf surfaces were generally free of debris and outer tissues layers were intact (A). After 133 days in 7 mm mesh bags in Hidden Creek, much of the epidermis had been lost (B) and leaf surfaces were colonised by bacteria and fine filamentous organisms, possibly Actinomycetes (C). After 238 days, most of the epidermis of leaves in 0.2 mm mesh bags had disappeared (D) exposing internal tissues to microbial colonisation (E). Bacteria were the main colonisers of intact epidermis (F).

A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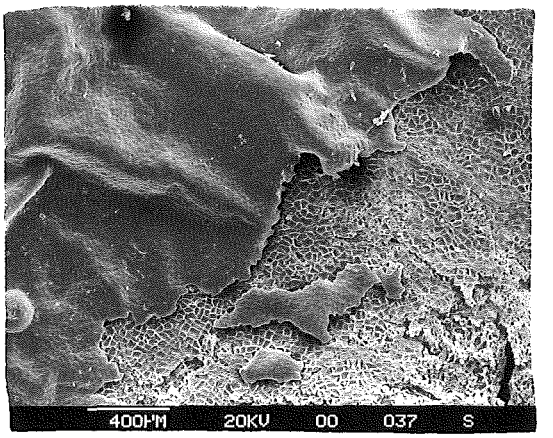
B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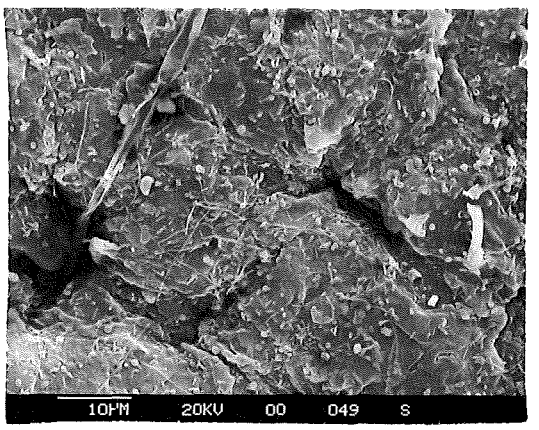
C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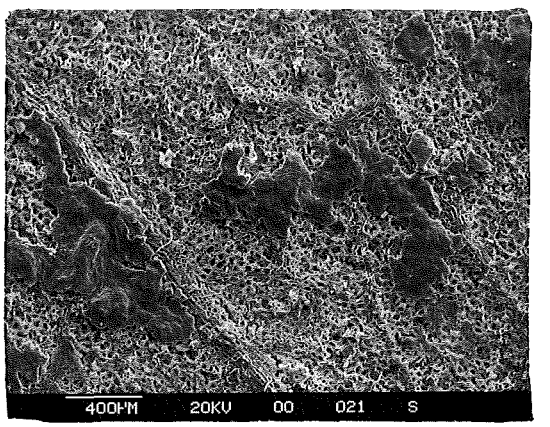
D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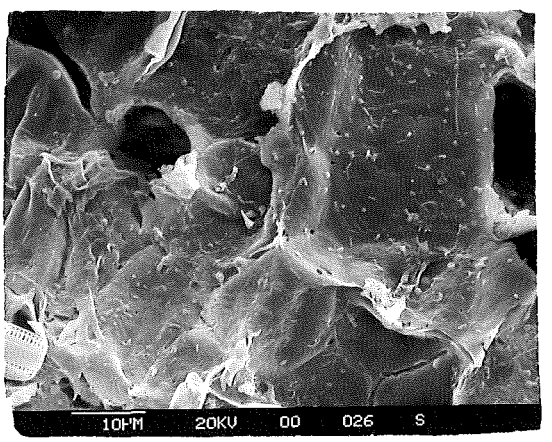
E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F

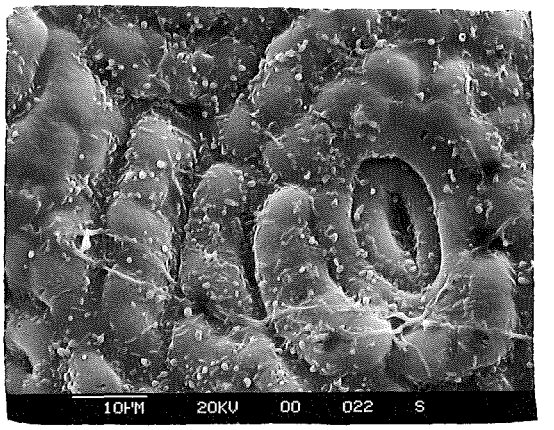
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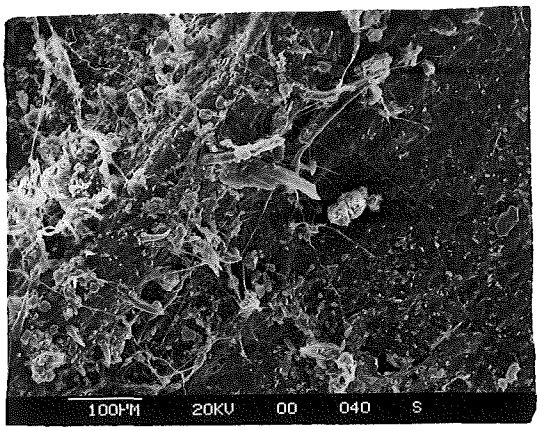
Plate 8.3. Scanning electron micrographs of kamahi leaf surfaces after 54-238 days immersion in Steep Creek (removed in January 1987). Leaves kept in 7 mm mesh bags in Steep Creek for 133 days were covered by amorphous material which was interwoven with fungal hyphae (A & B). No breakdown of the leaf surface was evident at this time (C). Surfaces of leaves kept in 0.2 mm mesh bags held in Steep Creek for 238 days were covered by high densities of fungal hyphae (D & E), but despite this, no signs of leaf breakdown were visible (F).

A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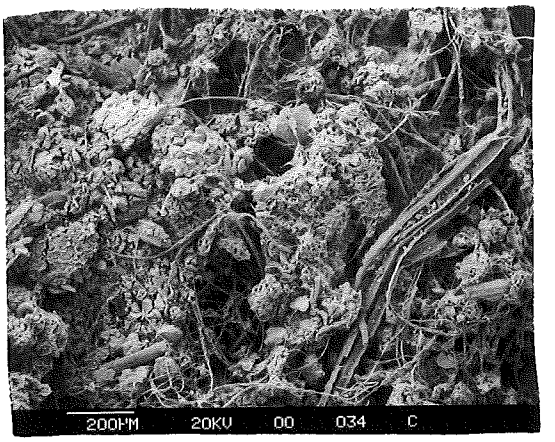
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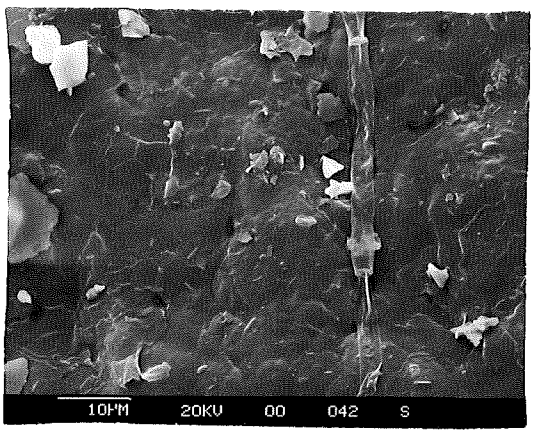
C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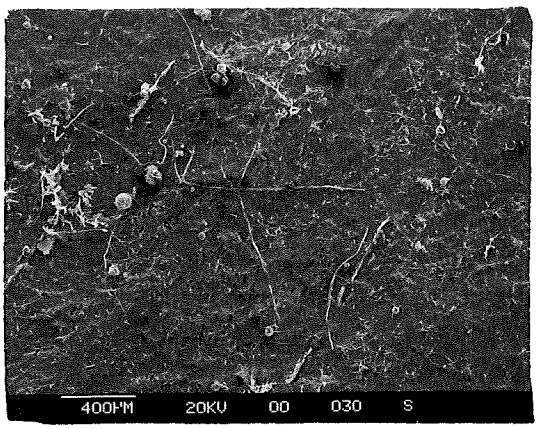
D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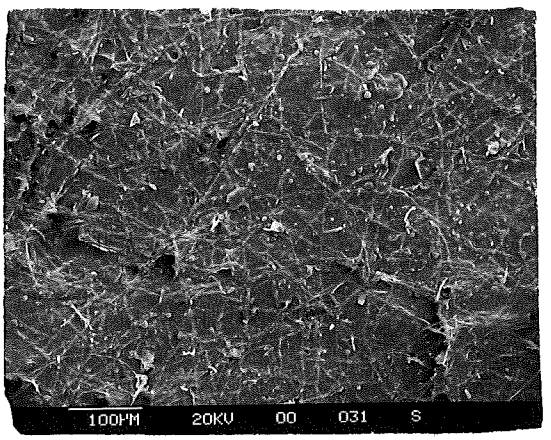
E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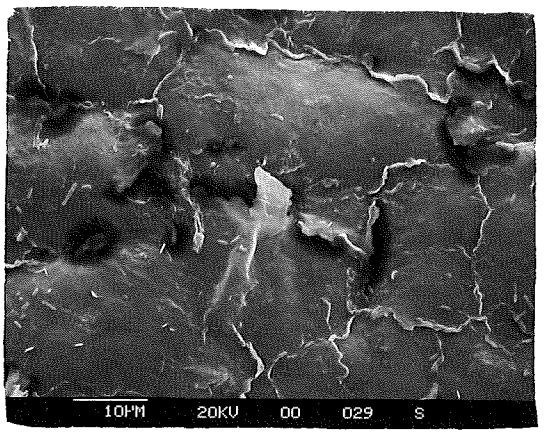
F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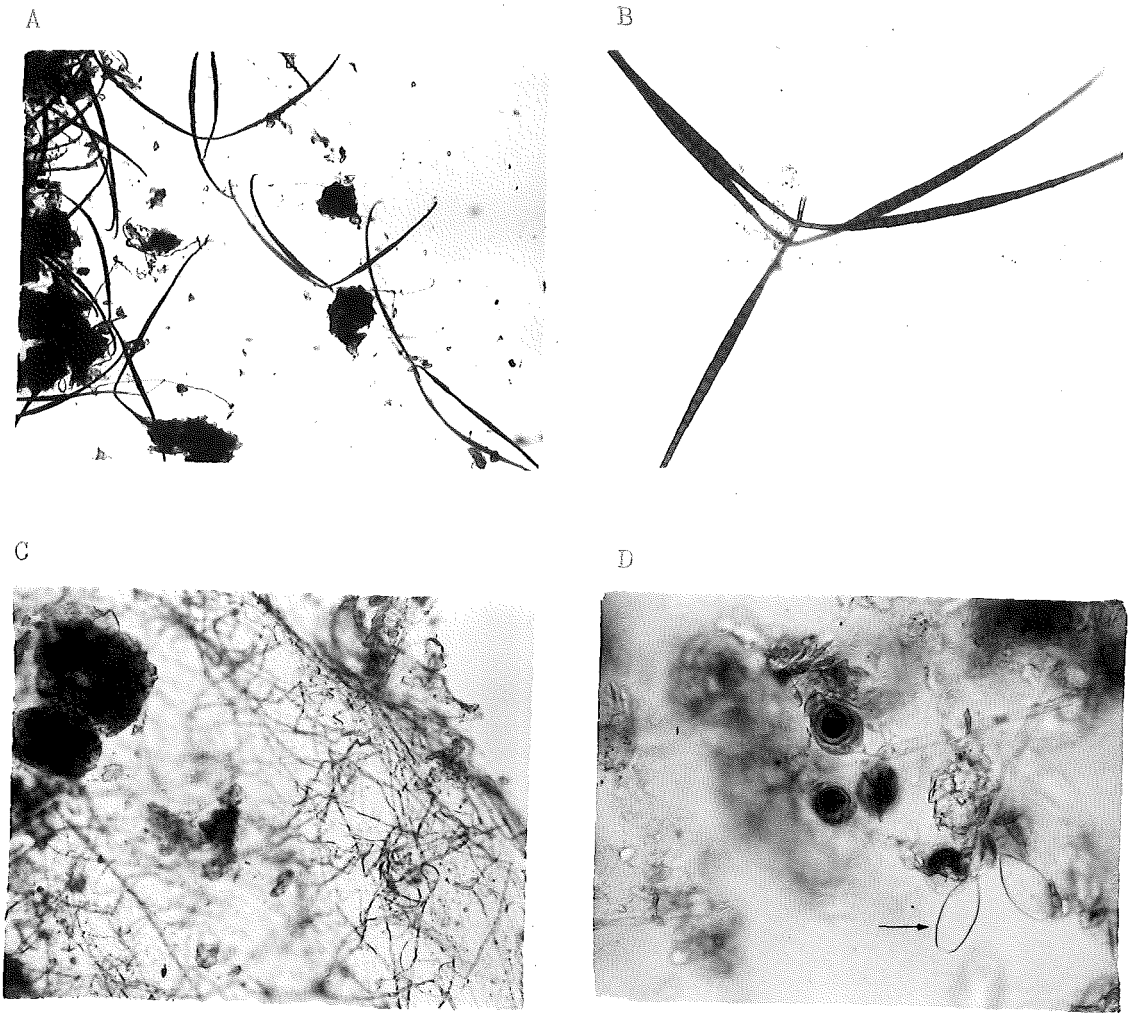

Plate 8.4. Fungi associated with surfaces of kamahi leaves held in leaf bags in Steep Creek. Spores of *Casaresia sphagnorum* (A & B) were abundant and appeared to be associated with a matrix of amorphous material attached to the leaf surface. Beneath this outer matrix was a layer of hyphae (predominantly *?Pythium* sp.) which often became detached when leaves were washed (C). D shows sporangia (arrow) typical of pythiaceous fungi (R.A. Aimer, pers. comm.).

Table 8.4. Total numbers (3 bags combined) of invertebrates found in 0.2 mm mesh bags filled with kamahi leaves and held in Hidden Creek or Steep Creek for 54, 133 and 238 days (removed in January 1987).

	Hidden			Steep		
	54	133	238	54	133	238
NEMATODA	4	15	3	0	0	0
ANNELIDA OLIGOCHAETA	2	0	3	1	0	0
ARTHROPODA ARACHNIDA ACARINA	0	2	0	0	0	3
CRUSTACEA COPEPODA HARPACTICOIDA	0	0	1	0	0	0
OSTRACODA	7	0	15	0	0	0
INSECTA EPHEMEROPTERA *Deleatidium* spp.	0	0	0	1	0	0
PLECOPTERA *Spaniocerca longicauda*	0	4	4	0	0	0
TRICHOPTERA *Philorheithrus agilis*	0	1	0	0	0	0
DIPTERA Chironomidae	24	122	53	61	76	67
Ceratopogonidae	0	1	0	0	0	2
Empididae	2	2	2	0	0	0

Table 8.5. Total numbers of invertebrates found in 7 mm mesh bags filled with kamahi leaves (no parentheses) or plastic strips (parentheses) and held in Hidden Creek or Steep Creek for 54, 133 and 238 days. Total numbers are for three bags combined except for Hidden Creek on day 238 (no parentheses) when only one bag had any leaf material remaining. The total % column expresses abundance as a percentage of total numbers for all dates combined.

	Hidden				Steep			
	54	133	238	Total %	54	133	238	Total %
NEMATODA	70 (11)	125 (25)	25 (105)	17.1 (22.4)	0 (0)	0 (0)	0 (0)	0.0 (0.0)
ANNELIDA								
OLIGOCHAETA	10 (1)	5 (4)	7 (17)	1.7 (3.5)	34 (0)	3 (1)	14 (1)	3.8 (0.6)
ARTHROPODA								
ARACHNIDA								
ACARINA	6 (0)	18 (5)	3 (3)	2.1 (1.3)	3 (1)	5 (0)	13 (12)	1.6 (3.9)
CRUSTACEA								
COPEPODA								
HARPACTICOIDA	219 (20)	282 (74)	2 (16)	39.1 (17.5)	0 (0)	0 (0)	0 (0)	0.0 (0.0)
OSTRACODA	34 (8)	32 (12)	6 (10)	5.6 (4.8)	7 (0)	0 (0)	1 (5)	0.6 (1.5)
INSECTA								
EPHEMEROPTERA								
Deleatidium spp.	8 (3)	11 (4)	3 (3)	1.7 (1.6)	0 (1)	0 (0)	3 (1)	0.2 (0.6)
Mauiulus luma	3 (1)	1 (0)	0 (0)	0.3 (0.2)	0 (0)	0 (0)	0 (0)	0.0 (0.0)
Nesameletus sp.	1 (1)	0 (0)	0 (0)	0.1 (0.2)	0 (0)	0 (0)	0 (0)	0.0 (0.0)
Ameletopsis perscitus	0 (0)	0 (0)	0 (0)	0.0 (0.0)	1 (1)	0 (0)	2 (3)	0.2 (1.2)
PLECOPTERA								
Austroperla cyrene	16 (6)	13 (3)	9 (6)	3.0 (2.4)	0 (0)	0 (0)	0 (0)	0.0 (0.0)
Cristaperla fimbria	0 (0)	8 (0)	0 (1)	0.6 (0.2)	0 (0)	0 (0)	0 (0)	0.0 (0.0)
Spaniocerca longicauda	1 (0)	2 (0)	0 (0)	0.2 (0.0)	0 (0)	0 (0)	0 (0)	0.0 (0.0)
Spaniocercoides cowleyi	0 (0)	0 (0)	0 (0)	0.0 (0.0)	0 (0)	0 (0)	0 (1)	0.0 (0.1)
Stenoperla maclellani	2 (3)	0 (1)	0 (7)	0.2 (1.7)	0 (0)	0 (0)	0 (0)	0.0 (0.0)
Zealandoblius confusus	0 (0)	0 (0)	0 (0)	0.0 (0.0)	3 (0)	1 (0)	1 (1)	0.4 (0.3)
TRICHOPTERA								
Rakiura vernale	0 (0)	0 (0)	0 (0)	0.0 (0.0)	3 (0)	0 (2)	2 (1)	0.4 (0.9)
Oeconesus sp.	1 (0)	0 (1)	0 (0)	0.1 (0.2)	0 (0)	0 (0)	0 (0)	0.0 (0.0)
Philorheithrus agilis	2 (1)	7 (2)	2 (2)	0.9 (0.8)	0 (0)	0 (0)	0 (0)	0.0 (0.0)
Olinga feredayi	5 (1)	5 (0)	0 (0)	0.8 (0.2)	0 (0)	0 (0)	0 (0)	0.0 (0.0)
Triplectides sp.	0 (0)	0 (0)	0 (0)	0.0 (0.0)	3 (0)	0 (0)	3 (0)	0.4 (0.0)
Zelolessica cheira	0 (0)	0 (0)	0 (0)	0.0 (0.0)	1 (0)	0 (0)	0 (0)	0.1 (0.0)
Polyplectropus sp.	0 (0)	0 (0)	0 (0)	0.0 (0.0)	0 (0)	0 (0)	1 (7)	0.1 (2.1)
Hydrobiosidae indet.	0 (0)	8 (1)	1 (0)	0.7 (0.2)	0 (0)	0 (0)	0 (0)	0.0 (0.0)
MEGALEPTOPERLA								
Archichauliodes diversus	0 (0)	0 (0)	0 (0)	0.0 (0.0)	0 (1)	1 (0)	0 (0)	0.1 (0.3)
COLEOPTERA								
Podaena sp.	0 (0)	0 (0)	0 (0)	0.0 (0.0)	0 (0)	0 (0)	4 (0)	0.3 (0.0)
DIPTERA								
Chironomidae	77 (24)	169 (132)	27 (100)	21.2 (40.6)	268 (77)	454 (40)	478 (169)	89.4 (85.1)
Ceratopogonidae	0 (0)	1 (0)	0 (0)	0.1 (0.0)	9 (0)	10 (0)	9 (7)	2.1 (2.1)
Empididae	31 (3)	25 (8)	1 (4)	4.4 (2.4)	3 (0)	0 (0)	3 (3)	0.4 (0.9)
Psychodidae	0 (0)	1 (0)	0 (0)	0.1 (0.0)	0 (0)	0 (0)	0 (0)	0.0 (0.0)
Hexatomini	0 (0)	0 (1)	0 (0)	0.0 (0.2)	0 (1)	0 (0)	0 (0)	0.0 (0.3)

*, Two subgroups (*myzobranchia* and *////*) were assumed to be present in Hidden Creek, but only the *////* subgroup was in Steep Creek (see Section 6.3.1.).

cyrene and *O. feredayi* larvae, both of which are known to eat leaves (see Section 8.2.2.), were usually much greater (up to 4.3 and 5.0 times, respectively) in bags containing leaves, and comprised relatively more of the total fauna than in bags with plastic strips.

In Steep Creek, faunas in all 7 mm mesh bags were dominated by chironomids which accounted for 85 to 89 % of total invertebrate numbers (Table 8.5.). Oligochaetes and mites were the only other taxa to represent more than 3 % of the bag fauna at this site. Some larvae of a *Triplectides* species, an obligate shredder, were found in two sets of 7 mm mesh leaf bags in Steep Creek, but were not recorded in bags containing plastic strips.

Invertebrate colonisation patterns

Mean numbers of invertebrates colonising 7 mm mesh leaf bags were always considerably higher (2.4-9.9 times) than numbers in bags containing plastic strips except in Hidden Creek when two of the leaf bags that had been immersed for 238 days were empty (Fig. 8.5.). In Steep Creek, mean numbers of invertebrates per leaf bag ranged from 112 to 178 and increased with time in the stream. In contrast, densities in Hidden Creek were highest on day 133 when an average of 236 animals were found in 7 mm mesh leaf bags. Invertebrate densities expressed per unit leaf weight (Fig. 8.5.) showed the same temporal patterns as those expressed as numbers per bag.

Food choice and ingestion rates of A. cyrene *larvae*

When offered a choice of conditioned leaves from Hidden Creek and Steep Creek and unconditioned (dried and leached) leaves, starved *A. cyrene* larvae clearly preferred to colonise leaves from Hidden Creek (Table 8.6.). Evidence of feeding was visible on leaf margins and was confirmed by the fact that unstarved larvae produced 2.4-3.5 times more faecal material when kept with leaves than plastic mesh (Table 8.7.). Interestingly, egestion rates (and by inference ingestion rates) of larvae were 1.5 times higher when feeding on Steep Creek leaves which were visibly tougher than Hidden Creek leaves. Only a minor proportion of the faeces in any treatment was composed of inorganic material (Table 8.7.).

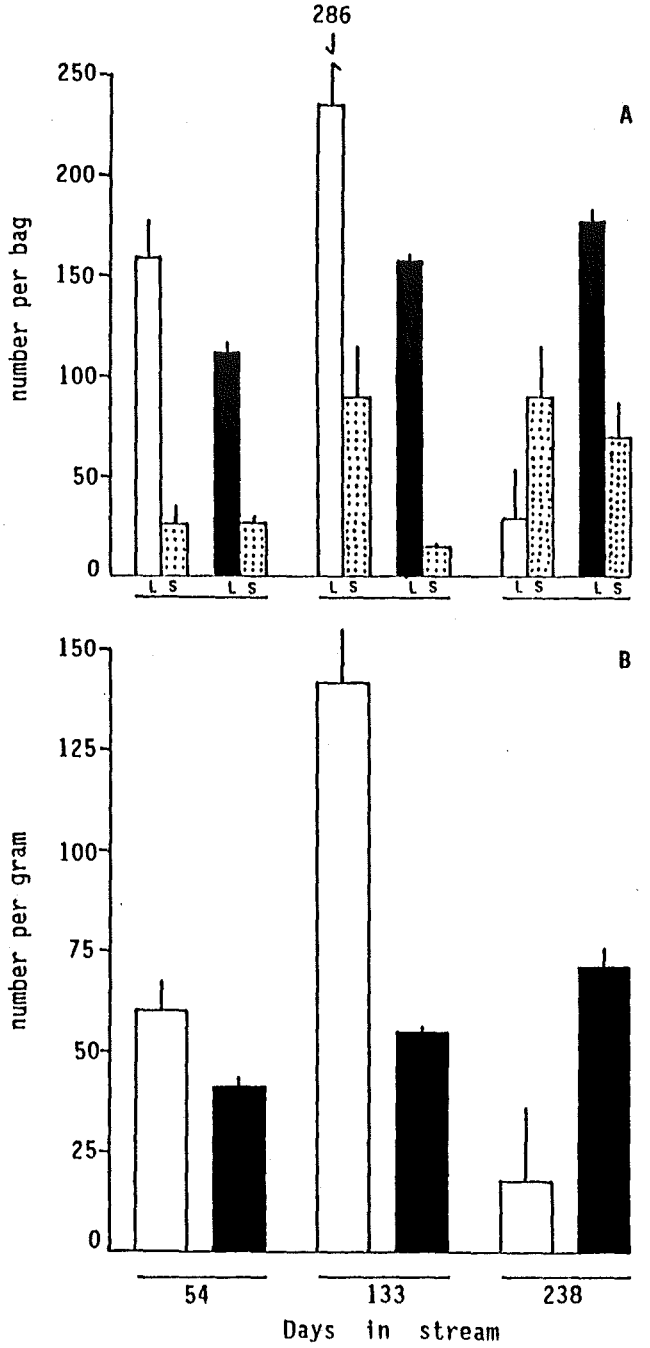

Figure 8.5. Numbers of invertebrates ($\bar{x}$ + 1 SE; n = 3) colonising 7 mm mesh bags held in Hidden Creek (open bars) and Steep Creek (closed bars) for 54, 133 and 238 days. A, numbers per bag. B, numbers per gram dry weight of leaf material remaining. L, bags containing leaves; S, bags containing plastic strips (stippled bars).

Table 8.6. Numbers of *A. cyrene* larvae ($\bar{x} \pm 1$ SE, n = 3) on kamahi leaves preconditioned in Hidden Creek or Steep Creek for 238 days or on unconditioned (dried and leached) leaves at hourly intervals in a food choice experiment.

	Hours		
	1	2	3
Hidden Creek	8.7 ±0.3	8.0 ±0.6	8.7 ±0.3
Steep Creek	0.3 ±0.3	0.7 ±0.3	0.3 ±0.3
Unconditioned	0 ±0	0.3 ±0.3	0 ±0

Table 8.7. Dry weight ($\bar{x} \pm 1$ SE, n = 3) and percent inorganic content of faeces produced by unfed *A. cyrene* larvae and by larvae fed leaves conditioned in Hidden Creek or Steep Creek for 238 days.

	Dry weight of faecal material ($g.g^{-1}dw.d^{-1}$)	% Inorganics
Unfed	0.044 ± 0.002	2.6
Hidden Creek	0.104 ± 0.019	0.9
Steep Creek	0.154 ± 0.017	3.3

8.5. DISCUSSION

Leaf breakdown rates

Breakdown rates of leaves in most bags at the four South Westland sites fell into the "slow" (-k < 0.0050) category of Petersen & Cummins (1974), but those kept in 7 mm mesh bags in Hidden Creek broke down at "medium" rates (0.0050 < -k < 0.0100). Indeed, -k values for kamahi leaves in all bags at the brownwater sites are amongst the slowest recorded for any tree leaves (Webster & Benfield, 1986). Half-lives of leaves kept in 0.2 and 1 mm mesh bags in Hidden Creek were similar to the half-lives of 231 and 155 days (0.2 and 1 mm mesh bags, respectively) estimated from weight losses of mountain beech leaves (*Nothofagus solandri* var. *cliffortioides*) kept in Middle Bush Stream, Cass (pH 6.7-7.1), although at that site half-lives in coarse mesh (3 mm) bags were only about half those found in 7 mm mesh bags in Hidden Creek (Davis & Winterbourn, 1977; Rounick & Winterbourn, 1983b).

Stream topography, temperature, discharge and aspects of water chemistry are known to affect leaf processing rates, either directly by physical breakdown or indirectly by influencing microbial activity and invertebrate feeding (Kaushik & Hynes, 1971; Petersen & Cummins, 1974; Boling *et al.*, 1975). In the preliminary study, leaf weight losses were considerably faster at the two clearwater sites than in the brownwater streams, and this pattern was confirmed subsequently in Hidden Creek and Steep Creek using bags with different mesh sizes. Discharge magnitude and variability were greater at the brownwater sites (see Tables 4.4. and 4.7.), and it is possible that leaf weight losses due to physical abrasion were higher in those streams. However, this seems unlikely to be important as the leaves were enclosed in bags. Because water temperature regimes were almost identical at three of the sites, this could not have had an over-riding effect on leaf processing rates.

Slow processing of allochthonous leaf litter in acid streams has been documented by many workers and most agree that a primary reason for this is low microbial activity at low pH (e.g., Mackay & Kersey, 1985; Allard & Moreau, 1986; Mulholland *et al.*, 1987). Breakdown rates of leaves kept in 0.2 and 7 mm mesh bags in Steep Creek were very similar, indicating that invertebrate feeding had negligible effects on leaf processing at that site. In contrast, the -k value for leaves held in 7 mm mesh bags was almost twice that for 0.2 mm mesh bags in Hidden Creek where feeding activities

of invertebrates (particularly *A. cyrene* and *O. feredayi*) apparently played a major role in leaf weight losses. Decay coefficients and half-lives of leaves in 0.2 mm mesh bags were higher in Hidden Creek than Steep Creek (particularly if day 0 was excluded from the calculations), suggesting that microbial decomposition of leaf litter was slower at the acid, brownwater site. However, some *Spaniocerca longicauda* larvae were found in fine mesh bags in Hidden Creek and weight losses of leaves in a given bag appeared to be related to the number of larvae trapped inside. Although nominally a fine-particle feeder, Davis & Winterbourn (1977) reported that a closely related species, *S. zelandica*, will ingest decomposing leaf tissue, so some of the leaf weight losses in fine mesh bags in Hidden Creek may be attributable to feeding by *S. longicauda*. Regardless of this, visual examination of leaves removed from 0.2 mm mesh bags indicated that microbial decomposition was much more advanced in Hidden Creek than Steep Creek by day 238.

Microbial conditioning

Aquatic fungi and bacteria can decompose allochthonous leaf litter through the macerating action of microbial enzymes which degrade epidermal and parenchymal cells, eventually leaving only lignified leaf skeleton (Suberkropp & Klug, 1981; Bärlocher, 1985). In general, fungal activity appears to be highest during the initial stages of decomposition, but as internal leaf surface area available for colonisation increases through microbial degradation and invertebrate feeding, it is thought that bacteria become more important (Kaushik & Hynes, 1971; Suberkropp & Klug, 1976, 1981). At the South Westland sites, no evidence of a fungal-bacterial succession was evident on kamahi leaves; bacteria were the most abundant microbial colonists at the circumneutral clearwater sites and fungi predominated on leaves at the acid brownwater sites. Several other workers have also noted high fungal biomass on organic matter in acidified waters (Hendrey *et al.*, 1976; van Frankenhuyzen & Geen, 1986), but Chamier (1987) reported significantly more aquatic hyphomycetes and bacteria on leaves from circumneutral (pH 6.6-6.8) than acid (pH < 5.5) streams in the English Lake District.

Respiration rates of leaf microflora measured on leaves from the South Westland sites (24.8-128.5 $\mu l.g^{-1}.h^{-1}$) are at the lower end of the range of those reported by Rounick & Winterbourn (1983b) for mountain beech leaves from Middle Bush Stream, Cass (70-210 $\mu l.g^{-1}.h^{-1}$). As mentioned in Section 8.3., such measurements on leaves from the brownwater sites probably

overestimated decomposer activity, because some fungi were associated with detrital accumulations on leaf surfaces and apparently were not involved directly in leaf breakdown. Bärlocher & Kendrick (1974) suggested that some aquatic fungi use leaves only as a substratum from which they may obtain nutrition from other leaf colonists, or more likely, from the surrounding media. The relatively high respiration rates on leaves from Hidden Creek on the first two immersion dates in 1986-87, and their subsequent decline, may reflect initial microbial breakdown of easily degradable leaf tissues (i.e., non-structural carbohydrates and protein) followed by slower decomposition of more refractory substances such as cellulose and lignin (Boling *et al.*, 1975; Allard & Moreau, 1986). The increase in oxygen uptake with time immersed in Steep Creek probably reflected progressive accrual of the fungal-detrital matrix on leaf surfaces.

Allard & Moreau (1986) found that oxygen consumption by leaves incubated in acidified (pH 4.0) water was significantly lower than by leaves kept in pH 6.2-7.0 water after about 70 days, but this phenomenon was not observed for leaves incubated at the South Westland sites. Some workers have suggested that, in recently-acidified waters, low pH can inhibit activity of leaf microfloras through aluminium toxicity or by affecting microbial physiology (Mulholland *et al.*, 1987; Palumbo *et al.*, 1987a), whereas Chamier (1987) proposed that acidification may disrupt microbial enzyme systems involved in leaf degradation. These mechanisms would not be expected in the South Westland brownwater streams where naturally high acidity has developed over a long period of time and microbes colonising leaves are those suited to the ambient water chemistry. Suberkropp & Klug (1981) suggested that humic acids may complex with organic leaf constituents (e.g., proteins) during decomposition and render them unavailable for microbial utilisation. If so, this process could account for at least some of the low microbial processing of leaves in acid brownwater streams where ambient DOC (and by implication humic acid) concentrations are high, and where leaf microbes may obtain a large proportion of their nutrition by direct uptake from the surrounding medium.

Colonisation and feeding by invertebrates

Numbers of invertebrates colonising 7 mm mesh leaf bags were generally higher in Hidden Creek than Steep Creek, and reflected the greater abundance of the benthos (see Chapter 6). However, not all invertebrates colonising bags would have fed directly on leaf tissue; some (e.g., hapacticoid copepods and nematodes) probably consumed microbes

growing on leaves. Others like *Deleatidium* spp. and some chironomids presumably ingested fine particulate matter trapped in bags, whereas hydrobiosid caddisfly larvae would have preyed on other bag colonists. Few large-particle detritivores colonised leaf bags at the acid, brownwater sites, but larvae of *A. cyrene* and *O. feredayi* which are known to eat leaves, were common in leaf bags at the clearwater sites and in Hidden Creek their feeding activities appeared to have a marked effect on leaf processing rates.

Many leaf-eating invertebrates are believed to prefer material with high microbial biomass since this can contain 2-4 times as much nutrient per unit weight as the average leaf (Kaushik & Hynes, 1971; Boling *et al.*, 1975; Bärlocher, 1985). In general, fungi are considered to be more nutritious foods than bacteria and several studies have shown that detritivores selectively feed on leaves colonised by different species of fungi (Suberkropp *et al.*, 1983; Arsuffi & Suberkropp, 1984; Bärlocher, 1985). In the present study, larvae of *A. cyrene* preferred to colonise leaves from Hidden Creek rather than leaves from Steep Creek or unconditioned leaf material, suggesting that Hidden Creek leaves were the most palatable. This need not reflect their nutritional value, however, and both assimilation efficiency and growth rate of the North American caddis *Clistoronia magnifica* were enhanced when larvae were fed leaves that had been conditioned at pH 4 rather than pH 6 (van Frankenhuyzen *et al.*, 1985; van Frankenhuyzen & Geen, 1986).

Lower palatability of leaves from Steep Creek could have been caused by release of antigustatory compounds (e.g., secondary metabolites) by fungi (see Arsuffi & Suberkropp, 1984), or more likely by lower nutritive value of the leaf tissue. At the brownwater sites, microbial conditioning of leaves appeared to be minimal and large surface accumulations of amorphous detritus would have been ingested with the leaf. Some workers have found that relatively high concentrations of metals such as aluminium accumulate on leaves in acid waters (Mulholland *et al.*, 1987; Palumbo *et al.*, 1987a), and although not investigated in the present study, precipitation or adsorption of metallo-organic complexes onto leaf surfaces could have augmented detrital accumulations on leaves at the brownwater sites, and contributed to their low palatability.

Finally, Anderson & Cummins (1979) suggested that some large-particle detritivores can compensate for poor food quality by increasing their ingestion rates. This phenomenon was observed in laboratory trials in which leaves from Steep Creek were ingested by *A. cyrene* larvae 1.5 times faster than leaves conditioned for an equivalent time in Hidden Creek. In

the field, the problem of leaf litter quality is likely to be real as the characteristic riparian vegetation of many brownwater streams is kamahi, manuka, rimu and tree fern (see Section 2.3.), all of which have tough, heavily-lignified leaves. In contrast, akeake, tutu, pate and wineberry were common alongside the clearwater streams and all have soft leaves which are likely to be more easily digested by detritivorous stream invertebrates. In South Westland, the retreat of glaciers has resulted in a succession of vegetation from podocarp-broadleaf forest on the lowlands to soft-leaved shrubs in glacial valleys. The presence of soft leaf tissue which is rapidly conditioned will be to the advantage of large-particle detritivores colonising streams where retention capacity is poor and litter inputs occur year round (e.g., Toilet Stream), and it can be expected to provide a highly stable and nutritious food source in streams where retention is good (e.g., Hidden Creek). Thus, the much higher densities of *A. cyrene* and perhaps *O. feredayi* larvae at the clearwater sites compared with the brownwater streams may well be attributable to the availability of a higher quality food source.

CHAPTER 9

SYNTHESIS

The primary aims of this study were twofold. First, I wanted to determine the effects (if any) of naturally low pH on benthic community dynamics in brownwater streams and compare these with changes observed in Northern Hemisphere clearwater streams acidified by atmospheric deposition. Acid rain is not a problem in New Zealand (Holden & Clarkson, 1986), and the acidity of brown waters is brought about mainly by high concentrations of dissolved organic acids of terrestrial origin. In Westland, South Island, brownwater streams with pH as low as 4 are common and these typically flow from wetland areas known locally as "pakihi". Because about half of recent pine forest plantings in Westland have been on pakihis (N.Z. Forest Service, 1984), my second aim was to assess the effects of forestry development on water chemistry (particularly DOC dynamics) and benthic invertebrate distributions in brownwater streams.

Effects of pH on benthic communities

In contrast to many Northern Hemisphere clearwater streams where acidification has become apparent only in the last few decades, the high acidity of brownwater streams in Westland is not a recent phenomenon. Although both types of stream typically have pHs in the range 4 to 5 and high concentrations of total dissolved aluminium (generally up to about 1000 $mg.m^{-3}$), a fundamental difference between them is the amount of aluminium present in the toxic labile (inorganic) monomeric form. In brownwater streams, most aluminium is complexed with organic matter and in this form it is essentially non-toxic. Concentrations of labile monomeric aluminium in eight streams with pH as low as 4.1 did not exceed 80 $mg.m^{-3}$, much lower than the 600 $mg.m^{-3}$ measured in some Northern Hemisphere streams with similar pH (Seip *et al.*, 1984; Bull & Hall, 1986). Labile monomeric aluminium concentrations greater than 100-200 $mg.m^{-3}$ are considered lethal to many fish species (Baker & Schofield, 1982; Mason & Seip, 1985), but few toxicity data are available for other animals. In laboratory trials, Clark & LaZerte (1985) found that as little as 10 $mg.m^{-3}$ of inorganic monomeric aluminium at pH < 4.4 reduced hatching success of the American toad, *Bufo americanus*, but preliminary work on invertebrates suggests that at least some can tolerate higher concentrations. Indeed, Havas and Likens (1985) found that aluminium (mostly as hydroxide complexes) did not become toxic to some species of Crustacea and chironomids until concentrations approached or exceeded 1000 $mg.m^{-3}$.

Invertebrate communities in acidified Northern Hemisphere streams typically have different taxonomic composition, fewer species and lower densities than nearby sites with circumneutral pH (Hall *et al.*, 1980; Townsend *et al.*, 1983; Mackay & Kersey, 1985; Simpson *et al.*, 1985). Mayflies are generally absent or poorly-represented in such streams and benthic communities dominated by stoneflies have been reported by some workers (e.g., Sutcliffe & Carrick, 1973). The causes of these changes are thought to include disruption of ionic regulation and calcium metabolism by hydrogen ions, mobilisation into the water column of high concentrations of toxic metals such as labile monomeric aluminium, and pH-related changes in the quality or quantity of food available (Haines, 1981). The relative importance of these mechanisms has not been resolved satisfactorily and although some workers have emphasised disruption of physiological mechanisms (e.g., Hall *et al.*, 1980; Allard & Moreau, 1987; Ormerod *et al.*, 1987), others have stressed the importance of changing food resources (e.g., Sutcliffe & Carrick, 1973; Otto & Svensson, 1983).

In acid brownwater streams draining undisturbed catchments in Westland, invertebrate communities are not taxonomically distinguishable from those in nearby circumneutral clearwater sites and most invertebrate taxa occur over a wide pH range with a lower limit of about 4.5. Fish are also common in these brownwater streams and six of 14 endemic freshwater species (in three families) known to occur in South Westland were recorded by Main *et al.* (1985) at pH < 4.8. Ball (1987) showed that the two species of New Zealand freshwater crayfish (*Paranephrops zealandicus* and *P. planifrons*) are physiologically better adapted to deal with the effects of low pH than most species of crayfish studied in the Northern Hemisphere. His work also revealed some intraspecific variability in acid tolerance whereby populations from very acidic habitats coped better physiologically with acid exposure than populations of the same species from less acidic waters. Thus, it is likely that many aquatic animals in Westland streams have broad habitat requirements that suit the wide range of physicochemical conditions encountered. In contrast, acidification of poorly-buffered Northern Hemisphere waters has been too rapid to allow sensitive species such as some fish, crustaceans and mayflies to adapt (Havas *et al.*, 1984), and marked deleterious effects on aquatic invertebrates have been reported at a pH as high as 6.0 (Haines, 1981; Dillon *et al.*, 1984).

Although the taxonomic composition of benthic invertebrate assemblages is not affected by low pH (above about 4.5), their densities were found to be much lower in acid brownwater streams. A major factor

contributing to this appeared to be the presence of poorer quality food at brownwater sites, and food quality and quantity along with low streambed stability were implicated in limiting annual biomass and production of *Deleatidium* populations in three South Westland streams. Studies of leaf litter processing rates and epilithon composition and structure in brownwater and clearwater streams showed that the nature of food resources available in these habitats differed considerably.

In acid brownwater streams, a large proportion of stone surface carbon was composed of abiotically adsorbed or precipitated DOC (i.e., non-cellular organic carbon), some of which was probably in the form of metallo-organic complexes, whereas epilithic carbon at nearby clearwater sites was primarily of algal origin. Although densities of fungi were sometimes high on leaves incubated in brownwater streams, they appeared to play an insignificant role in leaf breakdown and fungi were often associated with accumulations of amorphous material which adhered loosely to the surfaces of leaves. Slow microbial decomposition and the paucity of large-particle detritivores resulted in very slow breakdown of leaves in brownwater streams. In contrast, leaves in clearwater streams broke down much faster through the activities of microbes (mainly bacteria) and leaf-eating invertebrates (particularly the stonefly *Austroperla cyrene*) which were relatively abundant. In laboratory trials, leaves conditioned in a clearwater stream were ingested at much slower rates by *A. cyrene* larvae than leaves conditioned for the same length of time in a brownwater stream. Similarly, rates of grazing of epilithon by larvae of *Deleatidium* spp. (Ephemeroptera) were 2.2-16.8 times lower on stones taken from a circumneutral clearwater stream (pH 6.6-8.0) and material grazed contained proportionately less inorganics than grazed epilithon from an acid brownwater stream (pH 4.3-5.7). The faster ingestion rates exhibited by invertebrates when kept with decomposing leaves or epilithon from brownwater streams is interpreted as a response to their lower nutritive value and is in line with the predictions of Anderson & Cummins (1979) and Cummins & Klug (1979) that some benthic invertebrates attempt to compensate for low food quality by increasing their ingestion rates.

Overseas work has indicated that slow conditioning of allochthonous leaf litter and relatively high concentrations of abiotically adsorbed DOC may be typical of acid streams in general (e.g., Weber *et al.*, 1983; Mackay & Kersey, 1985; Winterbourn *et al.*, 1985; Allard & Moreau, 1986; Mulholland *et al.*, 1987). Nevertheless, larvae of the North American caddis *Clistoronia magnifica* grew faster on leaves kept in the laboratory at pH 4

than on leaves conditioned at pH 6, apparently because of greater availability of microbial and leaf derived energy at the lower pH. More research is needed into the quality and quantity of food available in anthropogenically and naturally acidified streams to resolve the question of potential food limitation.

Effects of catchment development on brownwater streams

North Westland streams that drain catchments developed for forestry and have pH as high as 5.2 contained similar numbers of benthic invertebrate taxa as undeveloped yet very acidic (pH ~4.1) sites draining directly from pakihi wetlands. However, they had only about half as many taxa as nearby streams that flowed through undisturbed catchments in native forest and had a pH > 4.5. Development *per se* did not change water pH or concentrations of toxic labile monomeric aluminium significantly, but did result in higher water temperature which was implicated as a potentially important factor contributing to low taxonomic richness where forest canopy had been lost. Although undeveloped pakihi streams with pH < 4.5 contained few invertebrate taxa, they did provide a favourable habitat for freshwater crayfish and the black eusirid amphipod, *Paraleptamphopus caeruleus*, which occurred there in large numbers but is uncommon in other environments. Congeneric taxa occur mainly in low and relatively constant temperature springbrooks, forest tributaries and subterranean waters (e.g., Chapman & Lewis, 1976; Winterbourn & Rounick, 1985), and the presence of a stable, low temperature regime is probably important for the maintenance of *P. caeruleus* too.

DOC export from three pakihi catchments in the Larry River Experimental Area near Reefton is amongst the highest recorded in the world (up to 37.75 $g.m^{-2}.y^{-1}$). Two years after crushing and burning of pakihi vegetation and of v-blading to improve drainage, DOC export had dropped by about 24 %, apparently through the removal or severe reduction of some sources of DOC (notably manuka forest) and alteration of catchment drainage characteristics. Considerable amounts of DOC appeared to originate within undisturbed and v-blade mound soils of developed catchments, but the one third of catchment area covered by v-blade tracks provided few potential sources of DOC. In-stream sources of DOC in the more recently developed catchment were also scarce, but in a catchment developed five years previously, there was considerable growth of vegetation in the stream channel (mostly *Sphagnum* moss) and this is believed to have contributed about 13 % of the DOC exported from that site. Recovery of

DOC dynamics to a pre-development (control) state was assisted by the retention of a buffer zone of manuka forest at the head of the catchment which contributed about 59 % of total vegetation inputs of DOC even though it comprised only 32 % of total catchment area.

The retention of strips of vegetation alongside the main drainage network is an effective way of keeping stream temperatures down and strips also serve as buffers against accelerated runoff and increased sedimentation. Jackson (1987) showed that in the year following v-blading of a Larry River catchment, sediment transport was an order of magnitude higher, and major floods three times more frequent than for an adjacent area of undeveloped pakihi. Future developers of pakihi catchments covered with manuka forest should also consider retaining an undisturbed portion of forest at the head of the catchment. This will help maintain natural DOC dynamics, conserve populations of crayfish and other animals (e.g., *P. caeruleus*) with specialised habitat requirements, and maintain a pool of invertebrate species that will be available for recolonisation following catchment development.

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APPENDICES

APPENDIX I

MAURI ORA, 1987, 14: 25-32

SPECTRAL PROPERTIES OF SOME WEST COAST WATERS AND THEIR RELATIONSHIP WITH DISSOLVED ORGANIC CARBON.

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ABSTRACT

Water samples were collected from 40 West Coast stream and river sites and analysed for dissolved organic carbon (DOC) and absorbance at 320nm. Extinction coefficients (E_{430}) and E_4/E_6 ratios were calculated for samples from 22 of these sites. DOC concentration ranged from 1.6-43.2g m^{-3} and was related linearly to absorbance at 320nm. The equation describing the relationship (DOC (g m^{-3}) = $34.98A_{1cm} + 1.55$) was comparable to equations found by other workers at similar wavelengths. A curvilinear relationship was found between DOC concentration and E_4/E_6 ratios (range 1.8-14.0) suggesting that proportionately more low molecular weight humic substances were present in brown waters than in clear waters. Extinction coefficients ranged from 0.0005 to 0.0047 and were correlated significantly with E_4/E_6 ratios indicating that low molecular weight humic substances absorbed more light per unit organic carbon than humic materials of higher apparent molecular weight.

KEY WORDS: Dissolved organic carbon, absorbance, extinction coefficient, E_4/E_6 ratio, aquatic humic substances

INTRODUCTION

In most aquatic ecosystems dissolved organic carbon (DOC) is the dominant form of organic carbon in the water column. A major fraction of DOC (50-75%) is made up of humic substances which generally are characterised as yellow-coloured, organic compounds (humic, fulvic and hydrophilic acids) that are refractory end products in the degradation of plant and microbial organic matter (Thurman, 1985). Natural DOC concentrations in streams and rivers normally range from 1-10g m^{-3}. However, concentrations in wetlands can be much higher (average 30g m^{-3}) because of the large net primary production of emergent plants and the presence of slow moving streams that leach vegetation and interstitial soil water (Thurman, 1985).

The colour of humic substances is caused by the presence of multiple bonds and unshared electron pairs in the molecular structure (Antherton et al., 1967; Orlov, 1972). Water colour can be measured spectrophotometrically and many workers have used absorbance of water at a specific wavelength as an index of DOC concentration (e.g., Banoub, 1973; Lewis and Canfield, 1977; Grieve, 1985). Absorption characteristics of humic substances also can be expressed by extinction coefficients and colour quotients (sensu Visser, 1984) such as E_4/E_6 ratios. Extinction coefficients give a measure of the degree of absorptivity per unit organic carbon and may be used to compare samples from different localities (Thurman, 1985). Colour quotients are related to the steepness of the slope in a spectrogram between two predetermined wavelengths and are usually independent of DOC concentration. E_4/E_6 ratios are believed to reflect particle size of the humic material and thus are indirect indicators of molecular weight (Chen et al., 1977).

In a recent paper (Collier, 1987) I assessed the utility of absorbance at 360nm as a measure of DOC concentration in 40 streams and rivers on the west coast of South Island, New Zealand. The present study examines other spectral properties (extinction coefficients and E_4/E_6 ratios) of water samples from some of these sites and evaluates the use of absorbance as an index of DOC concentration in the light of recent findings by other workers.

METHODS

SAMPLE COLLECTION:

Water samples (250mL, n=47) were collected from 40 stream and river sites on the west coast of South Island between February and May 1986. Sites 2,3, and 4 (Appendix 1) were the only streams sampled more than once. A brief description of the study area and map references of the sampling sites are given in Collier (1987). Samples were kept cool in the dark in polyethylene bottles until their return to the laboratory where they were filtered (0.45µm) and analysed, normally within one week of collection.

DOC ANALYSES:

Subsamples of water (50 or 100 mL) were evaporated to dryness and DOC concentration was determined by the micro dichromate oxidation procedure (Maciolek, 1962; 0.05N $K_2Cr_2O_7$, 0.03N $FeSO_4.7H_2O$) using heat by dilution (the heat generated on mixing sulphuric acid and the dichromate solution). DOC concentration was calculated according to the method of Maciolek (1962):

$$(1)\quad \text{DOC (mg)} = \frac{(A-B) \times N \times 8}{2.86}$$

where A= mL of ferrous sulphate used in blank titration
B= mL of ferrous sulphate used in sample titration
N= normality of ferrous sulphate
8= equivalent weight for oxygen
2.86= factor converting the weight of oxygen to organic carbon

Normality of ferrous sulphate was calculated by titration against the potassium dichromate solution:

$$(2)\quad N = \frac{\text{mL dichromate} \times \text{normality of dichromate}}{\text{mL ferrous sulphate used in titration}}$$

The technique was calibrated by ashing beech (Nothofagus) detritus and tannic acid (Mallinkcrodt analytical reagent) overnight at 500°C and comparing ash free dry weight with the amount of organic carbon extracted by dichromate oxidation. Organic matter was assumed to be 50% carbon (Maciolek, 1962).

SPECTROPHOTOMETRIC ANALYSES:

Absorbance spectra (200-650nm) of 4 representative water samples (Sites 3,10,29, and 37) and absorbance at 320nm (all samples) were measured using a Kontron Uvicon 860 spectrophotometer (1cm quartz cell). Absorbances of water samples from 22 of the sites were measured at 430, 460, and 660nm in a 10cm glass cell (Varian DMS 100 spectrophotometer). Distilled water blanks were used when making all absorbance measurements. E_4/E_6 ratios were obtained from the quotient of absorbance at 460 and 660nm and extinction coefficients were calculated by dividing absorbance at 430nm (per cm of cell path length) by the weight of organic carbon (g m^{-3}) in the sample. Gjessing (1974) proposed 430nm as a standard wavelength for comparing water colour. However, wavelengths used by other workers for calculating extinction coefficients vary from 400nm (Thurman, 1985) to 540nm (Visser, 1984).

RESULTS

DOC ANALYSES:

(a) Oxidation efficiency

Calibration of the heat by dilution dichromate oxidation procedure showed that it retrieved an average of 83% of the organic carbon in tannic acid and beech detritus (Table 1). Maciolek (1962) recommended immersing the acid/ dichromate mixture in a boiling water bath for 3 hours to facilitate maximum oxidation of the organic carbon. This step was omitted in the present study to enable rapid analysis of a large number of samples. DOC concentrations calculated from Equation 1 therefore needed to be multiplied by 1.20 to provide a more accurate estimate of total DOC (Table 1). The equation used to calculate DOC can be simplified to:

(3) DOC (mg) = (A-B) x N x 3.36

Lee et al. (1983) used heat by dilution dichromate oxidation to measure the organic carbon content of some South Pacific soils. They compared carbon values obtained by this method with estimates obtained using a high frequency induction furnace and found that corrections equivalent to those used in Equation 3 were necessary to give accurate estimates of organic carbon content.

(b) DOC concentrations in stream waters

DOC concentrations of water samples collected from the 40 sites ranged from 1.6 to 43.2g m^{-3} and were highest in streams draining pakahi (wetland) catchments in Larrys Creek Experimental Area (Sites 2-4), north of Reefton (Appendix 1). DOC concentrations at most sites (70%) were below 10g m^{-3} and at 48% of the sites were less than 5g m^{-3}.

SPECTROPHOTOMETRIC ANALYSES:

Absorbance (A) at 320nm was related linearly to DOC concentration (r^2=0.92). The relationship is expressed by the equation:

(4) DOC (g m^{-3}) = $34.98A_{1cm}$ + 1.55

Spectra of the four representative water samples all showed an increase in absorbance with decreasing wavelength (Fig. 1). The rate of increase was proportional to DOC concentration and was most pronounced in the ultra violet range of the spectrum (<360nm). Extinction coefficients at 430nm (E_{430}) for the 22 samples analysed ranged from 0.0005 to 0.0047 and 77% of the values were between 0.002 and 0.004 (Appendix 1). The lowest E_{430} and E_4/E_6 ratio were found in the water sample from Waiho River (Site 40) which drains Franz Josef glacier.

A curvilinear relationship was found between DOC concentrations and E_4/E_6 ratios (Fig. 2). All samples with ratios less than 7.0 had DOC concentrations below 5.2g m^{-3}. The highest ratios (13.5 and 14.0) were recorded in water samples from Sites 2 and 3 (L1 and L2, Appendix 1).

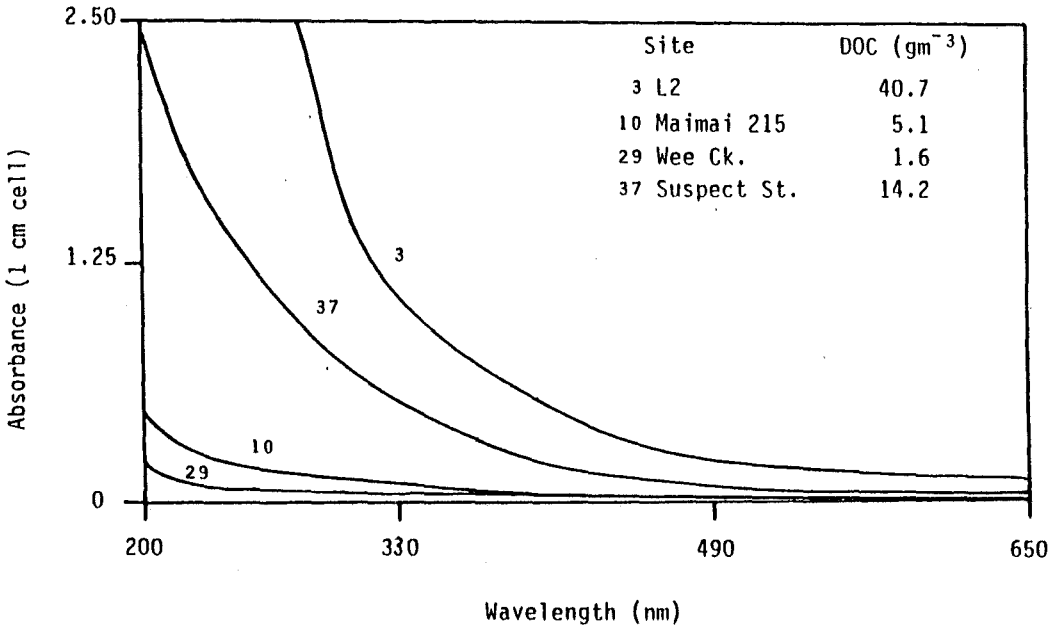

Fig. 1 Absorbance spectra of water samples from 4 sites with dissolved organic carbon (DOC) concentrations ranging from 1.6 to 40.7g m^{-3}.

DISCUSSION

Absorbance spectra for the four West Coast water samples resemble spectra obtained by Moore (1985) for peat water samples from northern Quebec, Canada. The undifferentiated nature of these spectra is the result of a multitude of overlapping excitation levels caused by very large numbers of chromophores in the humic molecule (Visser, 1984).

TABLE 1 Percent organic carbon recovered from tannic acid and beech detritus using heat by dilution dichromate oxidation. The right hand column gives factors by which organic carbon values obtained by the Maciolek (1962) calculation must be multiplied to correct for inefficiency in oxidation. AFDW = initial ash free dry weight of the compound oxidised.

Compound	AFDW (mg)	% recovery	Multiplication factor
Tannic acid	17.6	80.6	1.24
	20.0	85.1	1.18
	19.0	84.2	1.19
Beech detritus	28.7	86.2	1.16
	28.7	82.6	1.21
	28.7	79.1	1.26
± SD		83.0 ± 2.7	1.20 ± 0.03

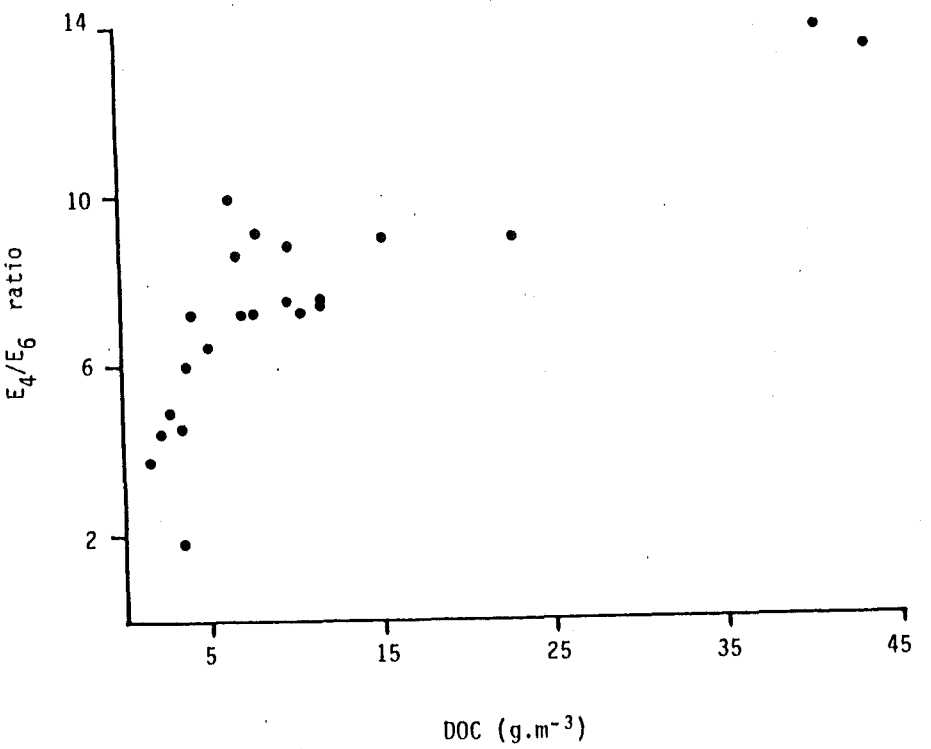

Fig. 2 Relationship between dissolved organic carbon (DOC) concentrations and E_4/E_6 ratios of water samples collected from 22 streams and rivers on the west coast of South Island.

Regression equations expressing relationships between DOC concentration and absorbance at 320 or 330nm in several studies including this one are given in Table 2. Slopes of all equations are similar (34.98-45.49) but intercepts vary from 1.39 to 7.46. The equation expressing the relationship between DOC concentration and absorbance at 360nm for Sites 1-40 is very similar to that given by Lewis & Canfield (1977) who measured absorbance at 360nm in some Venezuelan and southeastern United States waters (see Collier, 1987).

Chen et al. (1977) observed that water pH had a pronounced effect on E_4/E_6 ratios which reached maxima between pH 6 and 8. The pH of the West Coast water samples used to calculate E_4/E_6 ratios ranged from 4.1 to 7.8 (Appendix 1). In this pH range, Chen et al. (1977) showed that E_4/E_6 ratios changed by no more than 0.5 units and, thus, water pH is unlikely to have affected ratio estimates in the present study. Using a temporally extensive data set (24 weekly samples), Moore (in press) recorded mean E_4/E_6 ratios of 7.3 for Sites 5-10 and 11.1 for Sites 2-4. These compare favourably to 7.4 and 12.2, respectively, calculated from spot samples taken in the present study. Several workers have shown that E_4/E_6 ratios are related inversely to molecular weight of the humic material (Butler & Ladd 1969, Chen et al. 1977, Visser 1984). Thus, high ratios such as those recorded in samples from Sites 2 and 3 (13.5 and 14.0, respectively) infer enrichment by low molecular weight humic substances relative to samples with smaller ratios. Chen et al. (1977) recorded an E_4/E_6 ratio of 13.7 at pH 4 for a fulvic acid fraction with a molecular weight of 833, and all fractions with ratios less than 8 had molecular weights greater than 2109. Increasing DOC concentrations in the West Coast waters sampled appeared to be associated with decreases in the apparent molecular weight of the humic material.

TABLE 2 Details of dissolved organic carbon (DOC)/ absorbance relationships at 320 and 330nm from contrasting natural waters. A = absorbance in a 1cm cell.

Source	Wavelength (nm)	DOC range ($g\ m^{-3}$)	r^2	Equation (DOC ($g\ m^{-3}$)=)
This study	320	1.6-43.2	0.92	34.98A + 1.55
Gorham & Detenbeck 1986[1]	320	16.7-83.9	0.73	42.8A + 5.1
Moore 1985[2]	330	1-51	0.84	45.05A + 1.80
Moore in press[3]	330	2-18	0.92	45.49A + 1.39
Moore in press[4]	330	18-55	0.88	38.87A + 7.46

1 North American bog water
2 Canadian peat water
3 Sites 5-10 of this study
4 Sites 2-4 of this study

Stewart & Wetzel (1981) noted that dissolved organic matter (DOM) of low molecular weight absorbed consistently more light than DOM of higher molecular weight. They suggested that this was a function of molecular geometry whereby strongly absorbing hydrophilic groups of high molecular weight humic substances are restricted spatially to central portions of the molecule where their absorbing characteristics are masked partially by more external, lower-absorbing hydrophilic groups. However, Visser (1984) did not detect a significant relationship between absorbance per unit carbon (extinction coefficients) and molecular weight of aquatic humic substances from lakes, rivers, streams and swamps.

In the present study, extinction coefficients were related significantly to E_4/E_6 ratios ($r=0.56$, $P<0.01$), indicating that absorptivity was a function of the apparent molecular weight distribution of aquatic humic substances. Waters with high DOC concentrations had higher E_4/E_6 ratios and appeared to be dominated by lower molecular weight humic materials than clear waters where E_4/E_6 ratios were smaller.

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I thank Dr M.J. Winterbourn for driving the van and reviewing the manuscript and Dr T.R. Moore for introducing me to E_4/E_6 ratios. Rainer Putz and Dagma Ewald from Freiburg, West Germany, assisted with sample collection and the "Stream Team" provided valuable discussion. The study was funded by the University of Canterbury, National Water and Soil Conservation Authority and Forest Research Institute who also provided use of field facilities. The Chemistry Department kindly allowed me to use some of their equipment.

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APPENDIX 1 pH, dissolved organic carbon (DOC) concentrations, extinction coefficients (E_{430}) and E_4/E_6 ratios of water samples collected from 22 West Coast sites in February 1986. Grid references of sites are given in Collier (1987). -, unnamed streams.

Site no.	Name	pH	DOC ($g\ m^{-3}$)	E_{430}	E_4/E_6
1	Buller R.	6.2	2.3	0.0026	4.4
2	L1	4.1	43.2	0.0035	13.5
3	L2	4.1	40.7	0.0042	14.0
4	L3	4.3	22.9	0.0027	9.0
5	Maimai 205	5.7	11.5	0.0033	7.4
6	Maimai 207	6.1	10.4	0.0028	7.2
7	Maimai 208	5.8	9.6	0.0024	7.5
8	Maimai 209	6.0	7.0	0.0031	7.2
9	Maimai 214	5.8	6.8	0.0018	8.6
10	Maimai 215	5.8	5.1	0.0027	6.4
11	Inangahua R.	6.6	4.1	0.0033	7.2
22	Lankey Ck.	6.8	7.8	0.0030	7.2
26	Inangahua R.	6.2	9.7	0.0031	8.8
27	Rahu R.	6.4	3.6	0.0038	4.5
28	Inangahua R.	5.5	11.6	0.0030	7.6
29	Wee Ck.	7.5	1.6	0.0031	3.7
30	Lewis R.	7.1	2.8	0.0027	4.9
31	-	4.5	15.4	0.0047	9.0
32	Clear Ck.	6.5	3.7	0.0033	6.0
33	Hercules Ck.	5.1	8.1	0.0038	9.1
39	-	4.7	6.6	0.0043	9.9
40	Waiho R.	7.8	3.5	0.0005	1.8

APPENDIX II

New Zealand Journal of Marine and Freshwater Research, 1987, Vol. 21: 349–351
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Spectrophotometric determination of dissolved organic carbon in some South Island streams and rivers (Note)

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Abstract Absorbance at 360 nm and dissolved organic carbon (DOC) concentration were measured on 47 filtered water samples collected from streams and rivers of the west coast of South Island, New Zealand. The regression equation ($DOC\ (g\ m^{-3}) = 59.6\ Abs_{1\ cm} + 1.9$) calculated from the data, reliably predicted DOC concentration within the range 1.6–43.2 g m^{-3}. This relationship is similar to that found for some Venezuelan and south-eastern United States waters indicating that it may have widespread utility for estimating DOC concentrations in soft waters where DOC is dominated by humic substances.

Keywords dissolved organic carbon; DOC; absorbance; 360 nm; spectrophotometry; stream water; river water

Received 4 June 1986; accepted 17 September 1986

INTRODUCTION

Most conventional methods for measuring dissolved organic carbon (DOC) concentrations in fresh waters either require specialised equipment or involve time-consuming chemical oxidation procedures. An alternative technique is to measure the absorbance of water at a specific wavelength and to equate this to established DOC/absorbance relationships (e.g., Mackereth 1963; Banoub 1973; Lewis & Canfield 1977; Grieve 1985). Lewis & Tyburczy (1974) investigated the validity of these relationships obtained at a number of wavelengths, and concluded that absorbance at 360 nm provided maximum sensitivity and minimum variability. This paper evaluates the relationship between DOC concentration and absorbance at 360 nm in water samples varying widely in colour from streams and rivers of the west coast of South Island, New Zealand.

STUDY AREA

The study encompassed 40 stream and river sites which drained predominantly forested catchments located between 41° 50′ S and 43° 30′ S (Fig. 1, Table 1). Sites north of Greymouth were mainly in southern beech (*Nothofagus*) forest whereas most forests further south were mixed podocarp-hardwood commonly dominated by rimu (*Dacrydium cupressinum*) and kamahi (*Weinmannia racemosa*). Mixed podocarp forest occurs in the upper Grey Valley (Sites 5–10; Fig. 1), whereas Site 3 was in regenerating manuka (*Leptospermum scoparium*) forest, and some introduced conifers (*Pinus* spp.) were alongside Sites 2, 4, 9, and 31. Soils around sampling sites were predominantly yellow-brown earths (usually podzolised) and gley podzols, although recent organic soils were present alongside Site 38.

No significant point sources of pollution were evident on any streams or rivers except at Sites 24 and 25 which received coal mining effluent. Water at Sites 24 and 25 had very high conductivity (29.8 and 47.7 mS m^{-1} respectively) but no alkalinity, unlike the other sites where conductivity and alkalinity were positively correlated (Winterbourn & Collier in press). At 90% of these sites alkalinity was between 0 and 25 g m^{-3} $CaCO_3$ and conductivity ranged from 1.7 to 7.4 mS m^{-1}.

New Zealand Journal of Marine and Freshwater Research, 1987, Vol. 21

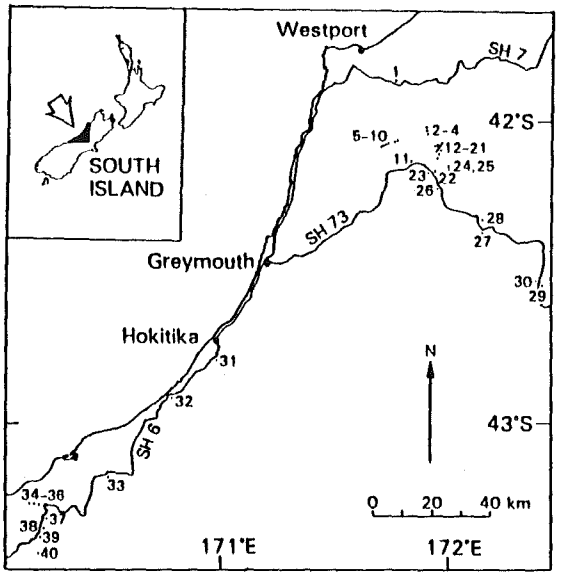

Fig. 1 Sites from which water samples were collected on the west coast of South Island, New Zealand. SH = State Highway. Names and exact locations of sites are given in Table 1.

Table 1 Names and map references of sites from which water samples were taken. —, unnamed streams.

Site	Name	Map ref. (NZMS 1)
1	Buller R.	S31 200612
2	L1	S38 377383
3	L2	S38 377381
4	L3	S38 377377
5	Maimai 205	S38 269328
6	Maimai 207	S38 274325
7	Maimai 208	S38 277324
8	Maimai 209	S38 279322
9	Maimai 214	S38 282318
10	Maimai 215	S38 286316
11	Inangahua R.	S38 323283
12	Lankey Ck	S38 368256
13	Lankey Ck	S38 364251
14	Lankey Ck	S38 363250
15	Ajax Ck	S38 363275
16	Ajax Ck	S38 362280
17	—	S38 363267
18	Murray Ck	S38 362267
19	—	S38 360266
20	—	S38 358267
21	—	S38 357266
22	Lankey Ck	S38 363249
23	Inangahua R.	S38 335280
24	Wellman Ck	S38 407233
25	Garvey Ck	S38 405235
26	Inangahua R.	S46 522073
27	Rahu R.	S46 560038
28	Inangahua R.	S46 552050
29	Wee Ck	S46 812904
30	Lewis R.	S46 811903
31	—	S57 522472
32	Clear Ck	S57 364336
33	Hercules Ck	S63 071989
34	Deep Ck	S71 847898
35	—	S71 860902
36	—	S71 864902
37	—	S71 885874
38	Mapourika Ck	S71 866831
39	—	S71 863806
40	Waiho R.	S71 825676

METHODS

Forty-seven water samples (250 ml) were collected in polyethylene bottles between February and May 1986. One sample was taken from each site except at Sites 2, 3, and 4 which were sampled two or three times. Samples were kept cool until their return to the laboratory where they were filtered (0.45 µm membrane filter) and analysed, normally within one week of collection. Aliquots of water, 50 or 100 ml, were used to determine DOC concentrations by the micro dichromate oxidation procedure described by Maciolek (1962) using heat by dilution. Results were calculated as oxygen consumed ($g\ m^{-3}$) and converted to DOC using an oxygen equivalent of 2.86 (Maciolek 1962). The technique was calibrated by ashing detritus and tannic acid and a multiplication factor of 1.20 was found necessary to adjust for inefficiencies in oxidation (Collier 1987). Absorbance of water at 360 nm was measured in a 1 cm cell on a Kontron Uvicon 860 spectrophotometer using a distilled water blank.

RESULTS AND DISCUSSION

DOC concentrations of water samples ranged from 1.6 to 43.2 $g\ m^{-3}$ and were related linearly to sample absorbance at 360 nm (Fig. 2). The regression equation describing the relationship is: DOC ($g\ m^{-3}$) = 59.6Abs + 1.9 (r^2 = 0.92).

When differences in cell path length are considered, this regression equation corresponds closely to that given by Lewis & Canfield (1977) (DOC ($g\ m^{-3}$) = 5.03Abs + 1.24) who used a 10 cm cell to measure absorbance at 360 nm in some Venezuelan and south-eastern United States waters. Their equation was calculated originally using data from only nine sites (seven streams, one river, one impoundment) with comparatively low DOC concentrations (3.3–15.7 $g\ m^{-3}$) (see Lewis & Tyburczy 1974). Grieve (1985) used Lewis & Canfield's (1977) equation to estimate DOC concentrations in

Note—Spectrophotometric DOC determination

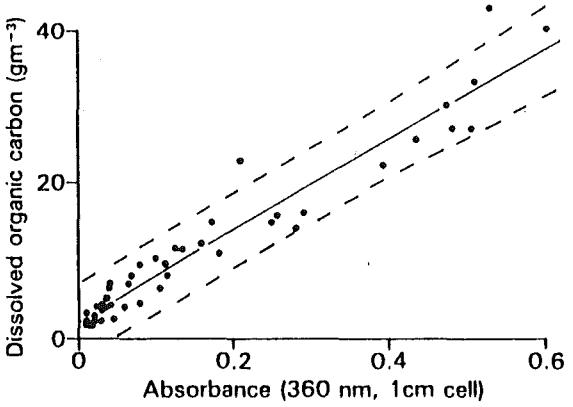

Fig. 2 Relationship between dissolved organic carbon concentration and absorbance at 360 nm for 47 water samples from 40 sites. The equation for the fitted regression line is 59.6 Abs + 1.9, $r^2 = 0.92$. Broken lines represent 95% confidence limits.

a small stream draining a grassy, moorland catchment in Scotland and suggested that their equation may have widespread validity. My findings support this contention and indicate that the relationship is linear up to at least 40 g m^{-3} DOC.

It generally is recognised that much of the colour in water comes from humic substances (mostly polymeric organic acids) leached from plant and soil organic matter (Thurman 1985). Stewart & Wetzel (1981) expressed concern that relationships between water colour and DOC may be affected by specific processes which alter the molecular weight distribution of dissolved organic matter (e.g., adsorption and precipitation of DOC with calcium, inputs of "new" leachate during periods of rainfall). Consequently, they proposed that DOC/absorbance relationships were likely to be valid only when applied to soft waters in which system-to-system differences in the age and origin of dissolved organic matter were minimised. In the present study, samples were taken from forested sites most of which had relatively low alkalinity and conductivity, similar to the Venezuelan waters sampled by Lewis & Canfield (1977). The broad geographic scope of the present study and the consistency of the findings with overseas work suggest that the DOC/absorbance equation established for west coast streams and rivers may have general application in soft waters where DOC is dominated by humic substances.

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APPENDIX III

Verh. Internat. Verein. Limnol.			Stuttgart, ■ 1987

Ecology of small streams on the west coast of the South Island, New Zealand

M. J. WINTERBOURN, K. J. COLLIER and A. K. GRAESSER

With 4 figures and 2 tables in the text

The west coast of the South Island is a high rainfall region bounded on the east by the Southern Alps. Numerous short, steep streams and rivers have their origins in the Alps and flow across the narrow coastal plain to the Tasman Sea. In many of the rivers, channel velocities are high and suspended sediment yields per annum are about ten times higher than world average rates for mountain areas (GRIFFITHS 1979). Precipitation occurs throughout the year but although common, storms are temporally unpredictable and monthly rainfall totals can vary considerably from year to year (Fig. 1).

Brown water streams are also a characteristic feature of several parts of Westland. Many drain pakihis, "a swampy acidic barren type of land" (HULME 1984) and the pH of stream water can be as low as 4 due to very high concentrations of organic acids leached from decomposing vegetation (COLLIER & WINTERBOURN in press).

Our recent studies have examined the effects of physical disturbance and acidification on benthic community dynamics, and the interrelationships between pH, dissolved organic carbon (DOC) concentration and aluminium speciation in streams unaffected by acid precipitation.

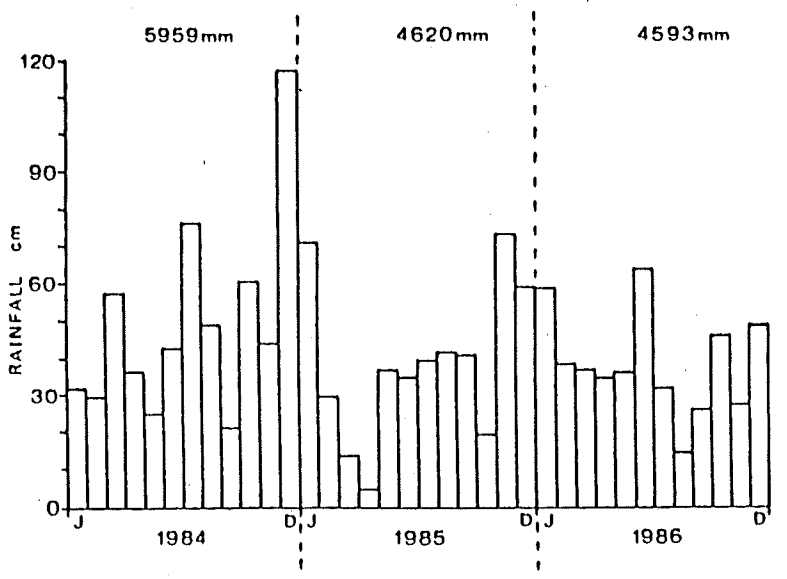

Fig. 1. Monthly rainfall at Franz Josef township, 1984—1986.

IX. Running Waters

Study sites and methods

We made surveys of clear and brown water streams in Westland and more detailed studies at seven contrasting sites on small streams (channel widths 1—5 m) in the Okarito—Franz Josef region (43° 20' S, 170° 12' E). All streams were located in at least partially forested (evergreen) catchments and had no apparent point sources of pollution or enrichment.

Physico-chemical and benthic invertebrate sampling methods have been described by COLLIER & WINTERBOURN (in press) and WINTERBOURN & COLLIER (in press). Estimates of benthic detrital biomass in 4 streams were obtained from bi-monthly sets of SURBER samples (0.2 mm mesh; 5 samples per set). Epilithic communities which developed on tiles and stones held in 7 streams for approximately 2-monthly intervals were examined with SEM. Their organic carbon (see COLLIER 1988), and chlorophyll-a content were determined and community respiration (CR) and net community primary productivity (NCPP) were estimated by measuring changes in oxygen concentration in still stream water at temperatures close to ambient. The effect of periodic exposure to air on epilithic algal biomass was examined by measuring the chlorophyll concentration on tiles held in three-tiered tile holders in two streams. A preliminary study of nutrient limitation of epilithic algae was made using a modification of the substrate-diffusion method described by PRINGLE & BOWERS (1984). Plankton netting (12.6 cm^2; 30 μm mesh) stretched over the mouths of 66 ml jars containing agar-nutrient mixtures (N, P, N + P; concentrations as used by PRINGLE & BOWERS) acted as diffusion-growth surfaces and were removed for extraction of chlorophyll.

Site numbers used to identify streams are those used by WINTERBOURN & COLLIER (in press).

Results and discussion

In 45 west coast streams, pH ranged from 4.1 to 8.1, $CaCO_3$ alkalinity 0—49 $g \cdot m^{-3}$, conductivity 2—97 $mS \cdot m^{-1}$ and DOC 1.8—41 $g \cdot m^{-3}$. Total reactive aluminium content of water ranged from 18 to 697 $mg \cdot m^{-3}$ but the toxic, inorganic monomeric species determined on 6 occasions at 4 chemically contrasting sites was always $< 50\ mg \cdot m^{-3}$.

Stone surface organic layers in acid, brown water streams (pH < 5, DOC > 9 $g \cdot m^{-3}$) consisted of an amorphous film of adsorbed organic matter overlain and embedded with filamentous green algae (*Tribonema*), *Fragilaria*, *Eunotia* and *Synedra*. However, at clear water sites (pH > 7, DOC < 2 $g \cdot m^{-3}$) epilithon was mainly Cyanophyta, *Achnanthes* and *Gomphonema* (COLLIER 1988). Algal biomass (as chlorophyll-a), epilithic CR and NCPP at the Okarito—Franz Josef sites (Fig. 2) were very low on a world scale (LOCK 1981, BOTT et al. 1985) and differences between sites could not be related to measured physico-chemical parameters, stream size or degree of canopy closure. Within sites, seasonal trends were not evident but rather discharge patterns (periodicity and intensity

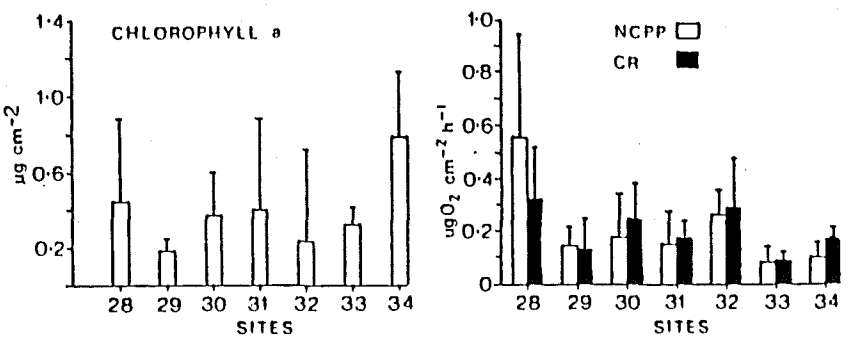

Fig. 2. Chlorophyll-a, net community primary productivity (NCPP) and community respiration (CR) of epilithon in 7 South Westland streams. Means (± 1 SD) of measurements in 3—6 months.

Table 1. Dry weights of particulate organic matter (POM) present in benthic samples from 4 South Westland streams. Means (± 1 SD) of n monthly collections.

Sites	POM (g dw · m^{-2})	n
28	26.5 (14.3)	10
30	20.3 (11.1)	5
31	13.2 (9.5)	10
32	15.9 (7.7)	9

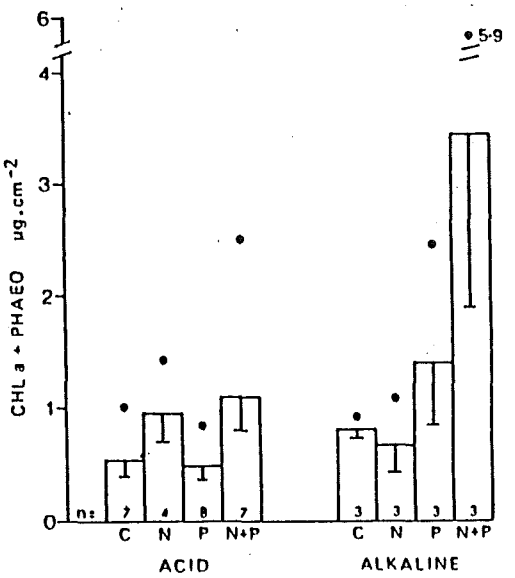

Fig. 3. Algal biomass (as chlorophyll-a + phaeophytin) on nutrient-diffusing substrata after 34 days in acid (pH < 5) and alkaline (pH 7.5) streams. Means ± 1 SE; ● = maximum biomass; n = number of substrata recovered for analysis. C = no-nutrient control, N = nitrogen added, P = phosphorus added, N + P = both nutrients added.

of flood events and stable low flows) appeared to be major factors affecting epilithic biomass (A. K. Graesser unpubl. data).

Periodic exposure of stone surfaces to air resulted in a reduction in the size of epilithic algal communities (Table 2) and is likely to play a significant limiting role in many west coast streams with their highly variable flows and shifting channels. In the substrate-diffusion experiment, epilithic algal biomass was increased by the addition of N and N + P in brown water streams and by P and N + P at the alkaline site (Fig. 3). These results suggest that whereas phosphorus may limit primary production in glacial valley streams, nitrogen may be limiting in brown waters where complexing with dissolved organics could reduce its availability to benthic algae.

Despite continuous inputs of riparian materials, standing crops of benthic detritus in four study streams were always very low (Table 1) and up to two orders of magnitude lower than annual means reported for some streams elsewhere (e.g. Minshall et al. 1983). However, they were comparable to post-flood levels reported by Rounick & Winterbourn (1983) for a South Island beech forest stream. The non-retentive nature of these streams reflects the frequent scouring of their beds by floods and the paucity of large wood debris in their channels.

Species richness and distribution of benthic invertebrates was not related to measured chemical parameters in 33 west coast streams above pH 4.5 (Winterbourn & Collier in

Table 2. Algal biomass (as chlorophyll-*a* + phaeophytin) on tiles held at 3 heights above the stream bed in 2 South Westland streams. Means (± 1 SD) for 2-monthly incubations measured in 8 months; n = 4–5 tiles per height per month.

Tile height	Pigment concentration ($\mu g \cdot cm^{-2}$) Site 28	Site 32
Lower (always submerged)	0.74 (0.63)	0.17 (0.10)
Intermediate	0.10 (0.11)	0.08 (0.07)
Upper (exposed during average flow)	0.08 (0.05)	0.02 (0.02)

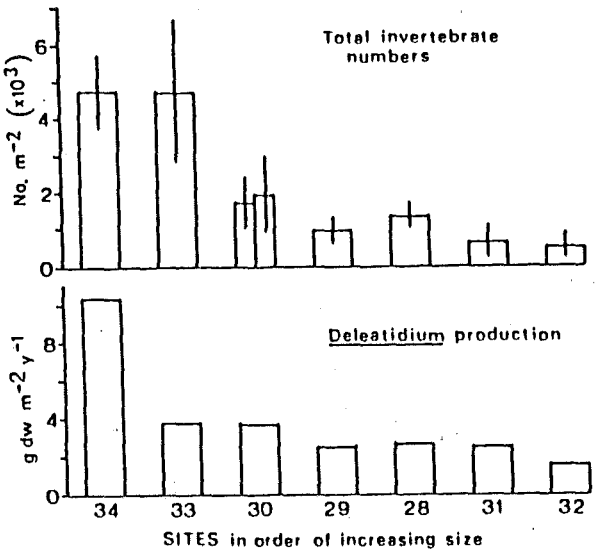

Fig. 4. Upper: Densities of benthic invertebrates (annual means ± 1 SD) in 7 South Westland streams. The two density figures shown for site 30 were obtained in separate sampling programs. Lower: Annual production of *Deleatidium* calculated by the size frequency method assuming a univoltine life history.

press). However, a significant positive correlation was found between numbers of taxa collected and channel stability as indicated by the stream bed component of the Pfankuch (1975) stability index which integrates measures of rock angularity, surface brightness, particle packing, scouring and deposition, and the presence of moss and algae. At most sites, Ephemeroptera and Plecoptera were numerically dominant with the leptophleiid, *Deleatidium* most abundant. Predators and collector-browsers which feed mainly on fine particulate detritus and epilithon are the predominant invertebrate functional feeding groups. Filter-feeders and shredders are poorly represented in these streams where the upper surfaces of stones are exposed to turbulent flows and frequent abrasion, and where retention of coarse particulate detritus is poor.

Mean annual density of macroinvertebrates ranged from 505 to 4720 m^2 at the 7 South Westland sites and was greatest in the smallest, most alkaline streams (Fig. 4). Differences in population densities between streams could not be attributed to measured physicochemical or biological parameters or channel stability, and fluctuations in numbers within streams were non-seasonal. Invertebrate drift densities were flow-dependent but always very low and unrelated to benthos density (Graesser 1988). Estimates of annual

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production for *Deleatidium*, the most abundant insect at all sites ranged from 1.2 to 10.4 g dw · m^{-2} · y^{-1} and showed a general decrease as stream size (channel width) increased. Thus, production was greatest in the smallest stream which is spring-fed, alkaline and has the least variation in discharge and water temperature.

In summary, the many physically unstable, flood-prone streams on the west coast of the South Island provide harsh environments for aquatic biota. Retention of particulate organic matter is poor and although streams are chemically diverse, primary (epilithic) productivity is generally low. Mayflies dominate most benthic faunas which have low-moderate densities and are characterized by limited feeding group diversity. Our inability to distinguish consistent temporal or spatial patterns in community structure and productivity among streams, is, we believe, a consequence of their highly variable and unpredictable discharge patterns.

Acknowledgements

We thank New Zealand Forest Service, the National Water and Soil Conservation Authority and the University of Canterbury for financial support of this project and the Forest Research Institute for use of their Okarito field station. Rainfall data were provided by the Westland National Park Board.

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APPENDIX IV

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Distribution of benthic invertebrates in acid, brown water streams in the South Island of New Zealand

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Abstract

Acid, brown water streams are common on the west coast of the South Island, New Zealand. Acid precipitation is not a significant problem in this region where stream water acidity is brought about by high concentrations of humic substances. The interrelationships between pH, alkalinity, conductivity, DOC and total reactive aluminium were investigated at 45 running water sites. pH (range 3.5 – 8.1) was strongly correlated with alkalinity (range 0 – 49 $g \cdot m^{-3}$ $CaCO_3$) and less strongly with conductivity (range 2.0 – 9.7 $mS \cdot m^{-1}$). A strong positive correlation was found between DOC and total reactive aluminium concentration both of which were correlated negatively with pH. In all brown water streams, most aluminium was probably in the non-toxic, organically complexed form. Benthic invertebrate assemblages were examined at 34 sites. Taxonomic richness was not correlated with pH and similar numbers of ephemeropteran, plecopteran and trichopteran taxa were taken from acidobiontic (pH $\leq$ 5.5), acidophilic (pH 5.6 – 6.9) and moderately alkaline (pH $\geq$ 7.0) groups of streams. Many species occurred over a wide pH range and had a lower limit of about pH 4.5. The mayfly, *Deleatidium* occurred at 33 sites and was amongst the five most abundant taxa at 32 of them. The stoneflies, *Zelandobius confusus, Austroperla cyrene* and *Stenoperla maclellani,* an elmid, *Hydora* sp. and a caddisfly, *Psilochorema* sp. also occurred in over half the streams and frequently were abundant. Few habitat specialists were found. Benthic assemblages were not associated strongly with measured physicochemical factors but streams in close proximity tended to have similar faunas. This suggests that the availability of suitable colonizers sets the limits to species richness and is important in determining the composition of benthic assemblages at a particular locality.

Introduction

The effects of acidification on the benthos and fish populations of running waters have been of increasing concern to biologists in recent years. Numerous authors (e.g. Sutcliffe & Carrick, 1973; Haines, 1981; Harriman & Morrison, 1982; Otto & Svensson, 1983; Townsend *et al.,* 1983; Kimmel *et al.,* 1985; Mackay & Kersey, 1985; Simpson *et al.,* 1985) have described reductions in species richness, density or diversity of invertebrates in acidified streams and rivers. The reasons are not well understood but are probably several and include disturbance of ion regulatory mechanisms and calcium metabolism, metal toxicity, and changes in the availability and quality of food.

In contrast to streams in which lowering of pH can be attributed directly or indirectly to acid precipitation, there have been few studies of the benthic fau-

nas of naturally acidic running waters. Exceptions are the work of Jones (1948) in south Wales and perhaps Otto & Svensson's (1983) study of brown water streams in southern Sweden, although anthropogenic sources may contribute to their acidity. Several low-gradient, black water rivers in the southern United States of America whose acidity is brought about by high concentrations of organic acids also have been the sites of recent investigations of macroinvertebrate production (Benke *et al.*, 1984, 1985; Smock *et al.*, 1985; Wallace & Benke, 1984). However, as they have predominantly sandy beds with woody snags providing their major stable substrata, they are difficult to compare faunistically with acidic, stony streams.

Acid rain is not a significant problem in New Zealand where the mean pH of rainfall is close to 5.6 (Holden & Clarkson, 1986). Deposition of acid sulphur on to the country is almost an order of magnitude less than on to Scandinavia and some 40 times less than in the worst affected areas of Europe. Nevertheless, on the west coast of the South Island of New Zealand, acid, brown water streams with stony beds are common. Their acidity results from high concentrations of humic substances (primarily humic and fulvic acids) derived from decomposing organic matter in soil and swamps by processes which are poorly understood (McKnight *et al.*, 1985).

The presence of numerous acid streams uninfluenced by acid precipitation provided an excellent opportunity to investigate the relationship between physicochemical factors, especially streamwater pH, and the distribution of benthic invertebrates. Previous biological studies in west coast streams have been concerned largely with the distributions of fish (McDowall *et al.*, 1977; Main *et al.*, 1985) and the annual migrations of commercially important whitebait larvae of endemic *Galaxias* species (McDowall & Eldon, 1980). The only ecological studies of stream invertebrates have been in Devils Creek, a clear stream with circum-neutral pH (Cowie, 1983, 1985; Winterbourn *et al.*, 1984), and in streams draining deforested catchments in the Maimai Experimental Area where the effects of forestry practices are being examined (Winterbourn & Rounick, 1985; Rounick & Winterbourn, 1986).

Study area

Westland is a narrow strip of coastal lowland mantled with coarse gravels, boulders and sand and bounded to the east by the main axial range, the Southern Alps. Being exposed to the prevailing westerly winds it is an area of high rainfall (1 500–7 000 mm per annum) which increases with altitude and distance from the sea. Natural vegetation below about 1 000 m is forest although on and near the coastal plain much of the original cover has been cleared for milling of timber and conversion to farmland (McCaskill, 1966).

Most forest streams in Westland carry very low sediment loads except for short periods during storm runoff (Pearce *et al.*, 1976; O'Loughlin *et al.*, 1978) and water varies from clear and colourless to deep brown with staining most intense in streams draining swamps, lakes and lowland forest (McDowall & Eldon, 1980). Streams included in our study all lay between 41°50′S and 43°30′S and drained predominantly forested catchments. North of Greymouth (Fig. 1) forests are mainly southern beech (*Nothofagus*) whereas further south they are mixed podocarp-hardwood forests commonly dominated by rimu (*Dacrydium cupressinum*) and kamahi (*Weinmannia racemosa*). Mixed podocarp-beech forest occurs in the upper Grey Valley (Sites 3–6, f, g; Fig. 1), whereas Site 2 is in regenerating manuka (*Leptospermum scoparium*) forest, and some introduced conifers (*Pinus* spp.) occur alongside the stream at Sites d, e, 5 and 25. The two stream sites (33, 34) close to the Franz Josef glacier are enclosed by low hardwood forest and subalpine scrub. No significant point sources of pollution were evident on any streams except at Sites 20 and c which receive coal mine effluent. Iron precipitates derived from abandoned gold mine workings were present on the stream bed at Site 10.

Because stream order, link number and catchment area could not be determined accurately from available maps, channel width was used as an indicator of stream size. Stream widths ranged from 0.5 to 5 m and with one exception (Site 32; 18°), gradients ranged from <1 to 8°. Four large river sites (1, 17, 18, 21) had channel widths from 12 to 40 m. Most streams and rivers had stony beds dominated by

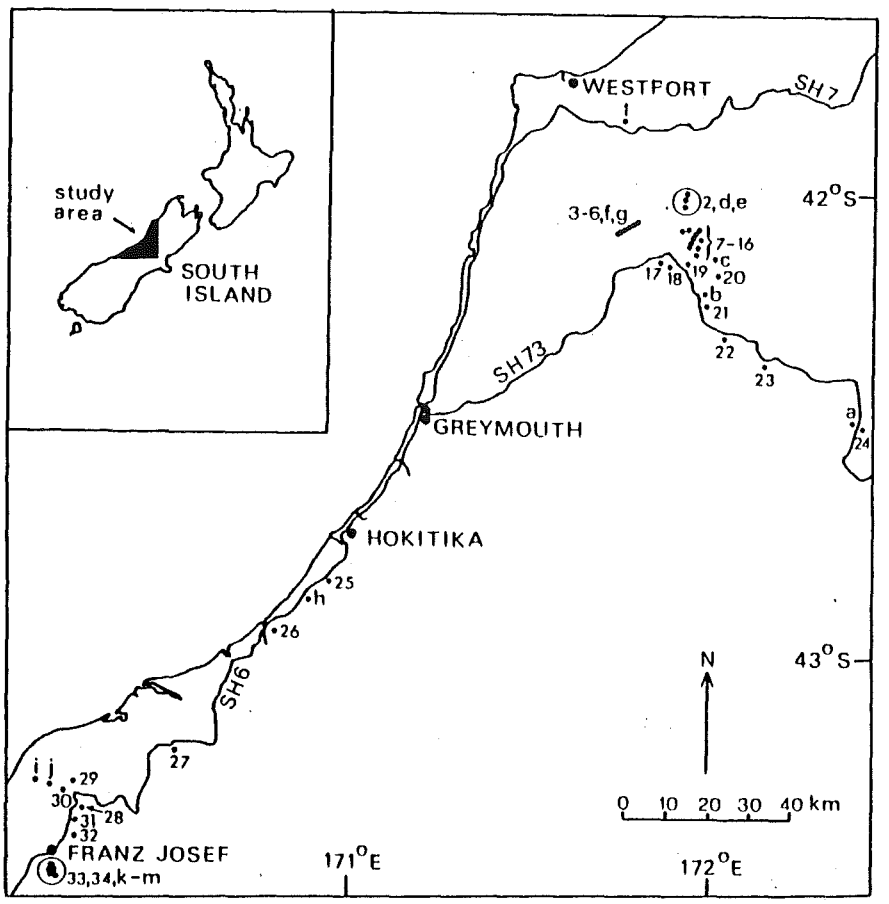

Fig. 1. Map of Westland showing locations of sites. Water and benthos samples were taken from Sites 1–34; water samples only from Sites a–m. SH = state highway.

coarse gravels and cobbles, and because of the region's high and frequent rainfall they are subject to rapid and frequent fluctuations in discharge. Many have physically unstable beds and banks as indicated by channel stability scores (Pfankuch, 1975) which gave 14 of 24 surveyed streams a fair or poor rating on a scale of excellent, good, fair and poor.

Methods

Field surveys were made in two successive summers (December 1984 and January 1986) when discharge of all streams was low. Physicochemical data were obtained from 28 streams in 1984 and from 43 (including 24 of those sampled the previous summer) in 1986 (Fig. 1). Sites were visited once during each survey.

Stream water pH was measured in the field or soon after with a Beckman portable meter and glass electrode whereas all other physicochemical measurements except aluminium were made on water samples returned to the laboratory in opaque, polyethelene bottles. Alkalinity was determined by titration with 0.025N HCl to pH 4.5 and conductivity was measured with a Radiometer CDM 2e meter. Subsamples of water for measurement of dissolved organic carbon (DOC) (25, 50 or 100 ml depending on suspected concentration) were passed through 0.45 μm Millipore filters, evaporated to dryness and analysed by dichromate oxidation (Newell, 1982) followed by titration with 0.03N $FeSO_4$. Calcula-

tion of DOC concentration incorporated a correction for inefficiency of oxidation as described by Collier (1987). Water used for aluminium determinations was filtered (0.45 μm) in the field, acidified to pH 1–2 with concentrated HNO_3 and analysed within 4 days. Total reactive aluminium was determined by atomic absorption spectroscopy (Varian Techtron) following complexation with 8-hydroxyquinoline and extraction with methyl isobutyl ketone (Barnes, 1975). In May 1986, stream channel stability was evaluated at 24 sites with the procedure of Pfankuch (1975) and pH of stream water was also measured.

The benthic invertebrate faunas of stony streams were sampled on the same days that physicochemical data were obtained. Twenty sites were included in the December 1984 survey and these plus an additional 14 sites were sampled in January 1986. Sites from which water samples but not fauna were taken were either too deep to sample or did not have stony beds. Collections of benthos were obtained by kick-sampling and brushing stones in front of a triangular net (0.2 mm mesh). Sampling was restricted to stony substrata where appreciable flow was present and was done in the same manner at all sites. Samples were preserved in the field and later all individuals were identified and counted. Identification was to operational taxonomic units (OTUs) which in most instances were species or probable (but unidentifiable) species. Exceptions were Chironomidae which were not separated below family, Oligochaeta which were uncommon and were mainly small Naididae, and the mayfly genus *Deleatidium*. The latter contains an unknown number of species most of which are unidentifiable as nymphs (Winterbourn & Gregson, 1981).

All correlation analyses involving fauna were made with data collected in January 1986, whereas data from both years were combined for making inter-site comparisons of faunal assemblages. Because many New Zealand stream invertebrates have poorly synchronized life histories and long flight or reproductive periods, sampling in summer can be expected to be as representative as at other times of years (Towns, 1985).

Results

Physicochemical factors

Stream water pH measured at 45 sites ranged from 3.5 to 8.1. Some intrasite variation was recorded in successive surveys (mean difference between surveys 1 and 2 = 0.6 units, maximum 1.1; surveys 2 and 3 = 0.2 units, maximum 0.6) but the rank order of sites on different occasions was almost the same (surveys 1 and 2, $r_s = 0.90$, $n = 24$; surveys 2 and 3, $r_s = 0.97$, $n = 22$). The lowest pH was recorded in water from a stream receiving coal mine effluent (Site 20) whereas the most acidic, undisturbed brown water stream had a pH of 4.1. pH was strongly correlated with alkalinity (Table 1) which ranged from 0 to 49 $g \cdot m^{-3}$ $CaCO_3$ and was highest in streams flowing over quartz-feldspathic schist in the Franz Josef glacier valley. Conductivity (range at unpolluted sites 2.0–9.7 $mS \cdot m^{-1}$ at 25 °C) also was correlated positively with pH although less strongly than alkalinity (Table 1).

Table 1. Correlation (r) between physicochemical parameters measured on Westland streams and rivers, December 1984 and January 1986. Data $\log_n$ transformed before analysis. All r values are highly significant ($p < 0.001$); $n = 62$ for all parameters except aluminium where $n = 37$.

	pH	Alkalinity ($g \cdot m^{-3}$ $CaCO_3$)	Conductivity ($mS \cdot m^{-1}$)	DOC ($g \cdot m^{-3}$)	Aluminium ($mg \cdot m^{-3}$)
pH	-	0.90	0.50	−0.81	−0.81
Alkalinity		-	0.56	−0.82	−0.86
Conductivity			-	−0.52	−0.68
DOC				-	0.88
Aluminium					-

Concentrations of DOC and total reactive aluminium were significantly and positively correlated with each other, but negatively correlated with pH, alkalinity and conductivity (Table 1). DOC concentration ranged from 1.6 to 43.2 $g \cdot m^{-3}$ and was highest in streams on poorly drained terraces (pakahis) either with *Leptospermum* forest (Site 2) or where the forest had been cleared and replanted with conifers (Site e). These streams also had the highest total reactive aluminium concentrations (up to 697 $mg \cdot m^{-3}$) whereas the lowest values (18–41 $mg \cdot m^{-3}$) were found in clear alpine and glacial streams (Sites 12, 24, 33, 34) with DOC concentrations < 4.2 $g \cdot m^{-3}$ and pH > 7.

Although not examined in the present study, aluminium speciation was investigated in a parallel study carried out at five contrasting sites (Sites 29, 30, 31, 33, 34). Bi-monthly sampling over a year indicated that most aluminium was in the organically complexed form at all times and that concentrations of the toxic, inorganic monomeric species were always < 50 $mg \cdot m^{-3}$ (Collier & Winterbourn, 1987). The strong positive correlation between DOC and total reactive aluminium concentration observed in the present study suggests that organically complexed aluminium predominated in most if not all of the brown water streams sampled.

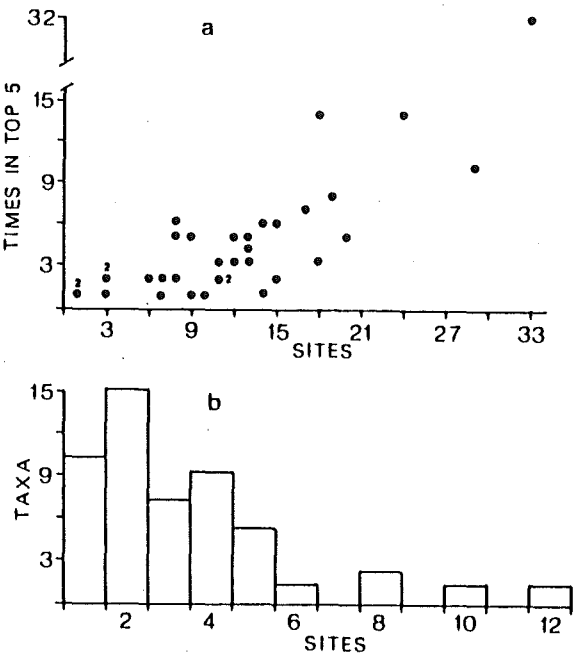

Fig. 2. The distribution of invertebrate taxa among 34 sites. a) the relationship between relative abundance and frequency of occurrence of common taxa. b) frequency of occurrence of uncommon taxa (those never one of the 5 most abundant at a site).

Benthic invertebrates

Ninety taxa (OTUs) were recognized in collections from the 34 stony stream sites, and of these all but nine were insects. Trichoptera, Plecoptera, Diptera and Ephemeroptera were best represented and accounted for 81% of all identified taxa (Table 2).

Frequency of occurrence of taxa is summarized in Fig. 2 which also provides a measure of relative abundance – the number of times a taxon was one of the five most abundant animals at a site. The most frequently occurring insects were the mayflies *Deleatidium* (33 sites) and *Nesameletus* sp. (17), an elmid beetle *Hydora* sp. (19), Chironomidae (18), the

Table 2. Numbers of taxa (OTUs) collected from 34 Westland streams.

pH range	Acidobiontic 3.5–5.5 (<4.5)		Acidophilic 5.6–6.9	Moderately alkaline 7.0–8.1	All streams
No. of streams	9	(5)	15	10	34
Ephemeroptera	6	(3)	8	7	11
Plecoptera	12	(7)	13	13	16
Trichoptera	15	(7)	22	22	31
Diptera	11	(9)	11	10	15
Others	9	(9)	13	11	17
Total OTUs	53	(35)	67	63	90

stoneflies *Zelandobius confusus* (24), *Austroperla cyrene* (20) and *Stenoperla maclellani* (29), and a caddisfly *Psilochorema* sp. (18). The first five of these feed predominantly on fine detritus and epilithon, and they were amongst the five most abundant taxa in over 40% of the sites where they occurred. By comparison, the facultative shredder *A. cyrene* and the predators *Psilochorema* and *S. maclellani* were in the top five only 25, 17 and 34% of the time, respectively. These eight taxa and a number of others appear to have broad habitat requirements, at least in terms of the physicochemical factors measured in this study and is illustrated in Fig. 3 where their distributions are shown in relation to pH.

In contrast to the common taxa, two groups with limited distributions were apparent. The first consisted of uncommon animals that were never amongst the five most abundant taxa at a site, whereas the second comprised a small number of "specialists" which were abundant at one or two sites (Fig. 2). The latter group included an amphipod, *Paraleptamphopus caeruleus* which was extremely abundant on *Sphagnum* and stones in *Leptospermum* forest at pH 4.1–4.4, *Pycnocentrella eruensis* a calocid caddisfly which appears to be restricted to small, headwater streams in beech forest (Cowie, 1985) and a helicopsychid caddis, *Rakiura vernale* that has a limited geographical distribution (Winterbourn & Gregson, 1981). The hydrobiid gastropod, *Potamopyrgus antipodarum* was a member of this group too, but it is widely distributed in lakes and low gradient streams and rivers elsewhere in New Zealand, particularly in non-forested catchments.

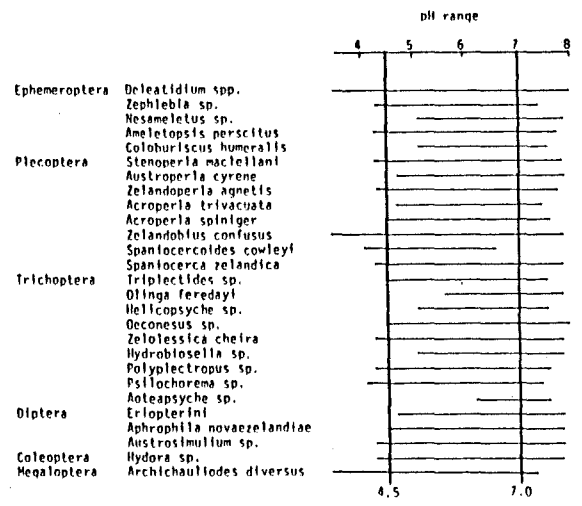

Fig. 3. The distribution of 27 taxa in relation to stream water pH. Only taxa found at a minimum of 8 sites are shown.

Faunal assemblages

Numbers of taxa taken at individual sites ranged from 5 to 36. Taxonomic richness was not correlated significantly with stream water pH (January 1986 rank order of sites; $r_s = 0.02$, $p > 0.05$), and the numbers of taxa from acidobiontic (pH ≤ 5.5), acidophilic (pH 5.6–6.9) and moderately alkaline (pH > 7.0) streams were 58, 67, and 63, respectively (Table 2). However, the numbers of ephemeropteran, plecopteran, and trichopteran taxa taken at the five most acidic sites (pH < 4.6) was only half that at the other four acidobiontic sites (Table 2) suggesting that a pH of about 4.5 represents the lower limit for a number of species.

As with pH, neither stream width nor Pfankuch stability score was correlated significantly with numbers of taxa ($P > 0.05$) but a significant negative correlation ($r_s = -0.42$, $P < 0.05$) was found with the streambed component of the stability score. This indicates that in general fewer taxa were present where stream beds consisted of rounded, poorly packed, shifting materials with little clinging algae or moss (Pfankuch, 1975).

To compare stream faunal assemblages, Sorensen's index (Southwood, 1978) was calculated for all site pairs and the similarity coefficients obtained were clustered using the hierarchical average-linkage procedure of Bridges (1966). Clusters were differentiated weakly (Fig. 3) and rather than being defined by unique groups of taxa they represented different combinations of OTUs drawn from a common pool. Thus, the five main groups of sites distinguished at the 0.48 level of similarity in Fig. 4 each contained 30–50 taxa out of a possible 90, and inter-group similarity coefficients ranged from 0.39 to 0.70 (Table 3). Groups had overlapping physicochemical characteristics (Table 3), but sites in close proximity tended to cluster together although not necessarily to the exclusion of others. Five tributaries of Murrays Creek made up cluster E, four adjacent streams

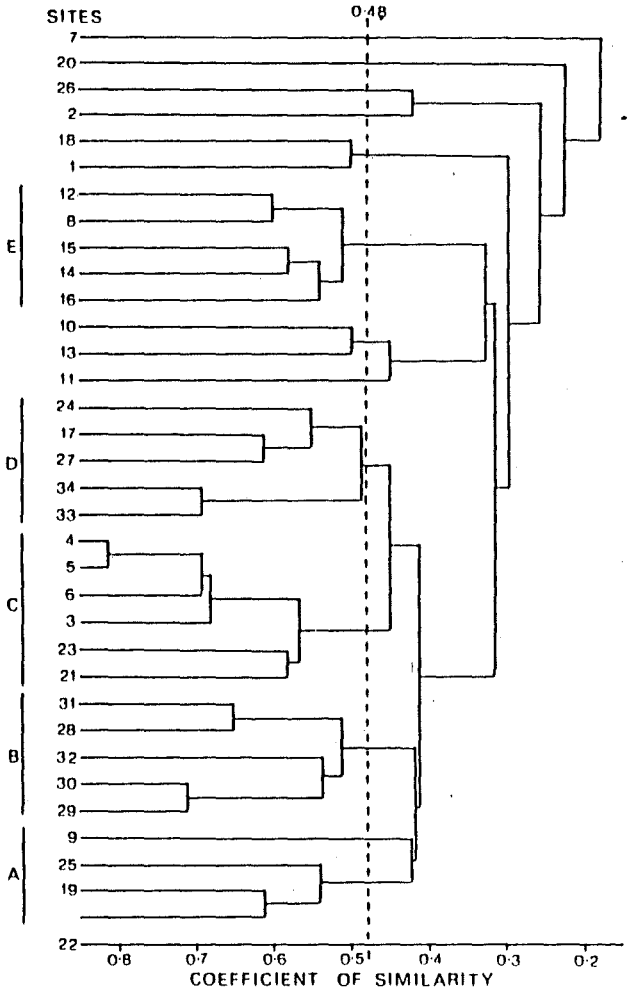

Fig. 4. Site clusters obtained using Sorensen's coefficient of similarity calculated from invertebrate presence-absence data. Characteristics of clusters A–E are summarized in Table 3.

in the Maimai Experimental Area were included in cluster C, and southern brown water streams made up cluster B. On the other hand, clusters A and D comprised more widely separated sites. It should also be noted that of the last four sites to be clustered (i.e. those with the greatest faunal dissimilarity), three had highly acidic waters (pH <4.5) and the other (Site 26) had the most unstable bed of all the streams examined.

Discussion

Brown water streams on the west coast of the South Island are characterized by low conductivity and alkalinity, and their colour and acidity result from the presence of organic acids derived from decaying vegetation. In these respects they resemble black and brown water streams and rivers in many tropical and temperate regions (Hynes, 1970; Naiman, 1982; Dudgeon, 1982). Colour (abs 360 nm) and DOC concentration are strongly correlated in Westland streams ($r^2 = 0.97$, n = 47; Collier, 1987). The maximum DOC value we recorded (43 $g \cdot m^{-3}$) is near the middle of the range of concentrations reported by McKnight *et al.* (1985) for a *Sphagnum* bog (24–62 $g \cdot m^{-3}$) and lower than maxima of 62 $g \cdot m^{-3}$ and 47 $g \cdot m^{-3}$ given by Gorham *et al.* (1984) for surface bog waters and waters draining peatlands in North America.

According to Hall *et al.* (in press), experimental acidification of small streams with HCl to pH

Table 3. Characteristics of the five main clusters of streams distinguished in Fig. 4. Similarity in taxonomic composition is expressed by Sorensen's coefficient.

Clusters		A	B	C	D	E
Width (m)		2.2 – 4	2.5 – 5	0.3 – 12	1 – 30	0.6 – 1.7
pH range		4.5 – 7.4	4.3 – 6.4	5.8 – 6.4	5.1 – 7.9	7.1 – 7.4
DOC ($g \cdot m^{-3}$)		3.3 – 15.4	4.1 – 14.9	3.6 – 9.7	1.6 – 8.1	1.9 – 3.7
No. of taxa		50	47	47	48	30
Coefficients of similarity	A	–	0.62	0.62	0.63	0.40
	B		–	0.70	0.69	0.39
	C			–	0.69	0.52
	D				–	0.54
	E					–

5.25 – 5.5 did not noticeably affect the behaviour of aquatic insects, but in conjunction with aluminium additions (208 $mg \cdot m^{-3}$) it did. Consequently, they suggested that fluctuating aluminium concentrations in low-order streams at pH 4.5 – 5.5 may be a primary factor affecting invertebrate biology. Although total reactive aluminium in New Zealand streams with a pH < 5.5 ranged from 294 to 697 $mg \cdot m^{-3}$, the results of an intensive study in a subset of streams (Collier & Winterbourn, 1987) indicates that concentrations of the toxic, inorganic monomeric species are likely to be considerably < 50 $mg \cdot m^{-3}$.

Contrary to the results of several Northern Hemisphere studies in regions affected by acid rain (e.g. Mackay & Kersey, 1985; Simpson *et al.*, 1985), reduction in pH of stream water was not paralleled by a reduction in invertebrate species richness until about pH 4.5. Furthermore, ephemeropteran, plecopteran and trichopteran taxa were just as well represented in moderately alkaline, acidophilic and acidobiontic streams down to this pH. The finding of no correlation between species richness and pH in stony streams is consistent with the hypothesis of Hall *et al.* (in press) and the suggestion of Mackay & Kersey (1985) that the ability of some mayflies and stoneflies to survive in highly coloured waters may be the result of chelating properties of humic acids which bind toxic metal ions mobilized at low pH.

One reason for the absence of taxa from some acid waters is that their eggs are unable to develop or hatch, e.g. the snail, *Physa heterotropha* at pH 4 (Burton *et al.*, 1985). However, this need not be so, and eggs of the caddis, *Clistoronia magnifica* developed normally at pH 4 (van Frankenhuyzen *et al.*, 1985). Alternatively, unsuccessful attempts at colonization by winged stages have been suggested as reasons for the absence of *Baetis* and *Rhithrogena* species (Ephemeroptera) from acid waters (Harriman & Morrison, 1982), and adult behaviour during oviposition by *Baetis* was implicated by Sutcliffe & Carrick (1973). Little is known about colonization or ovipositional behaviour of New Zealand stream insects, although McLean (1967) observed four species of mayfly in the families Leptophlebiidae, Siphlonuridae and Oligoneuriidae oviposited in flight. If this is the normal method of egg laying for members of these families in New Zealand, then it is unlikely that water testing methods such as those proposed for *Baetis* can account for the absence of genera such as *Zephlebia, Nesameletus* and *Coloburiscus* from some streams of low pH.

Rather, the pool exhaustion hypothesis discussed in this context by Hildrew *et al.* (1984) may provide a better explanation for the distributional patterns of taxa among streams. That is, the availability of suitable colonizers sets the limits to species richness at a particular locality and defines in part the composition of benthic assemblages. It can be argued that the tendency of contiguous streams to have similar faunas provides support for this hypothesis, although they also may have other features in common that complicate the issue. The biology and dispersal characteristics of the aerial stages of aquatic insects are poorly known and difficult to study. However, a knowledge of them is essential if we are to develop a more complete understanding of aquatic insect distributions and colonization dynamics.

Lastly, some authors have noted shifts in trophic diversity and in the relative proportions of different functional feeding groups or feeding guilds associated with streamwater pH. For example, Townsend *et al.* (1983) found that only shredders, collectors and predators occurred at most acid sites in the Ashdown Forest, southern England, whereas they were joined by grazer-scrapers and filter-feeders at more basic sites. Mackay & Kersey (1985) found that shredders were dominant in the most acidic streams in southern Ontario whereas collectors were relatively more abundant at higher pH. Otto & Svensson (1983) recorded a positive correlation between pH and numbers of shredder and scraper species but not other functional groups in southern Sweden.

Differences in the nature of the food resources available, a likely consequence of acidification have been proposed as a reason for such shifts in representation of various feeding guilds (Winterbourn *et al.*, 1985; Hall *et al.*, in press). However, the accuracy of functional group designations has been questioned by Hawkins *et al.* (1982) who suggested that the foods and feeding methods of many aquatic insects are likely to be more varied than such classifications acknowledge. We agree with this with respect to the west coast stream fauna, many members of which

are herbivore-detritivores that are not easily typecast as shredders, scrapers or collector-grazers as indicated by other New Zealand studies (see Winterbourn *et al.*, 1984 and references therein). Therefore, we have not presented our results in terms of feeding guild representation.

In an earlier study (Rounick & Winterbourn, 1982), a common core of invertebrate taxa (genera and/or species) were shown to be abundant and widely distributed in stony streams varying in size, substratum stability and riparian vegetation in various parts of New Zealand. Members of this common core were well represented in the brown water streams of Westland at least above pH 4.5, and in even more acid water in the case of *Deleatidium*. Fish also are common in these acid streams and six of 14 endemic, freshwater species (in three families) that occur in south Westland were recorded by Main *et al.* (1985) at a pH <4.8.

Havas *et al.* (1984) pointed out that "brown-water lakes and streams have distinctive flora and fauna that differ considerably from those of recently acidified clear-water lakes." Faunal comparisons cannot be made in New Zealand between streams affected by acid rain and naturally acidified streams. However, our study shows that at pH >4.5, faunal assemblages in brown water streams have similar species richness and taxonomic composition to those in clear water streams of circum-neutral pH elsewhere in the region.

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APPENDIX V

LABORATORY STUDIES OF INVERTEBRATE pH TOLERANCE

INTRODUCTION

Bioassays were carried out on selected benthic invertebrates from circumneutral clearwater streams to investigate whether brown water and low pH were directly toxic to them.

METHODS

Bioassays were conducted from December 1985 to January 1986, and again from February to May 1986 under controlled laboratory conditions (6°C, 12 h light/dark cycle). The first trial assayed larvae of the mayflies *Deleatidium* spp. and *Nesameletus* sp. collected from Cave Stream in mid Canterbury (NZMS1 S66 200003), and *Olinga feredayi* (Trichoptera) larvae from Kaituna River on Banks Peninsula (NZMS1 S94 040285). The second trial used *Deleatidium*, *O. feredayi* and *Austroperla cyrene* (Plecoptera) larvae collected from Hidden Creek, a circumneutral clearwater stream in South Westland (see Fig. 2.3.).

Wherever possible, similar-sized larvae of each taxon were selected for bioassays on each date. In the laboratory, larvae were placed in plastic containers with 1 mm mesh bottoms (10 larvae of each taxon per container) and sets of three containers (one for each taxon) were immersed in four types of water: clear water and brown water each with pH adjusted to "acid" (mean pH 4.2-4.5) and "circumneutral" (pH 7.2-7.7) levels with KOH or HCl. In the first bioassay, distilled water was used initially as the clearwater medium, but artesian well water was substituted after twelve days. Water collected from Toilet Stream (South Westland) served as clear water in the second trial, whereas Steep Creek (South Westland) was the source of brown water for both bioassays. All water types were aerated continuously with bubblers and larvae were fed leaves (mainly *Schefflera digitata*) conditioned in Hidden Creek; leaves were renewed periodically.

In the first bioassay, larval mortalities were monitored daily for 14 days and then once every two days for 32 days. In the second trial, larvae were examined every 1-2 days for 30 days, and at 4-6 day intervals for a further 56 days. On observation days, all dead larvae were removed from containers, and water pH was read (Metrohm E488 meter) and adjusted if

necessary. After about two weeks of both trials, fungi were seen growing on *O. feredayi* larvae kept in Steep Creek water, especially at low pH. In the first trial, a fungicide (Actidione (Upjohn)) was added (5 $\mu g.l^{-1}$) to containers of Steep Creek water to reduce the problem, but this was not necessary in the second trial because fungal growths were less extensive.

RESULTS

First bioassay

Deleatidium larvae died rapidly after the first three days of the experiment with 100 % mortality occurring in both clear waters and acid brown water within 11 days (Table 1.). However, mortality rates were much lower in circumneutral brown water where the last larva had died by day 28. *Nesameletus* sp. larvae were slightly more tolerant of the experimental conditions than *Deleatidium* spp., and most survived for at least the first eight days of the experiment (Table 1.). Mortality rates were initially fastest in circumneutral clear water and slowest in circumneutral brown water, but by 20 days 80-100 % of *Nesameletus* sp. larvae had died in most treatments. No *O. feredayi* larvae died in any treatment in the first 17 days of the first bioassay (Table 1.). Thereafter, mortality rates were slowest in acid clear water where 60 % of *O. feredayi* larvae were still alive by the end of the experiment (46 days). *O. feredayi* mortalities were initially fastest in circumneutral clear water, but after about 36 days, they were exceeded by rates in both brown waters in which all larvae had died by days 38 and 40.

Second bioassay

As in the first trial, *Deleatidium* larvae died rapidly after 2-3 days with 80 % mortality occurring between days five and nine in all treatments (Table 2.). *O. feredayi* larvae showed a similar response to that observed in the first assay with few ($\leq$ 10 %) dying before day 23. Indeed, no *O. feredayi* larvae died in circumneutral brown water in the first 49 days of the trial. By the end of this experiment (86 days), 40-50 % of the larvae were still alive in all treatments except in acid brown water where 90 % mortality had occurred. *A. cyrene* larvae survived well in all water types and few mortalities were recorded in the first 49 days of the assay. No larvae of *A. cyrene* died in circumneutral clear water (Table 2.). After 49 days, death rates were almost identical in acid clear water and both brown

water treatments and between 40 and 50 % mortality had occurred by the end of the assay (86 days).

CONCLUSION

Although experimental conditions in these experiments were not ideal for larvae (particularly *Deleatidium* spp.), results do show that both *A. cyrene* and *O. feredayi* collected from circumneutral waters can survive for considerable periods at low pH.

Table 1. Numbers of larvae of three invertebrate taxa surviving in four types of water in the first assay. Coefficients of varation of pH measurements (means shown) ranged from 2.8 to 7.6 %

Deleatidium spp.

	Clear water		Brown water	
Days	pH 7.2	pH 4.3	pH 7.2	pH 4.2
0	10	10	10	10
1	10	10	10	10
2	10	10	9	10
3	8	10	9	9
4	6	10	8	7
5	3	7	8	5
6	2	6	8	2
7	0	2	8	1
8	0	2	8	0
10	0	1	8	0
11	0	0	7	0
12	0	0	5	0
13	0	0	4	0
14	0	0	3	0
17	0	0	3	0
20	0	0	2	0
22	0	0	1	0
26	0	0	1	0
28	0	0	0	0

Nesameletus sp.

	Clear water		Brown water	
Days	pH 7.2	pH 4.3	pH 7.2	pH 4.2
0	10	10	10	10
1	10	9	10	10
2	10	9	10	10
3	10	9	10	10
4	9	9	10	10
5	8	9	9	10
6	8	9	9	10
7	8	9	9	10
8	7	9	9	10
10	6	9	9	10
11	2	5	9	9
12	2	4	9	9
13	2	3	9	8
14	1	2	9	7
17	1	2	9	3
20	1	2	8	0
22	1	2	8	0
24	1	2	6	0
26	0	2	4	0
28	0	2	1	0
30	0	1	0	0
38	0	1	0	0
40	0	0	0	0

Olinga feredayi

	Clear water		Brown water	
Days	pH 7.2	pH 4.3	pH 7.2	pH 4.2
0	10	10	10	10
17	10	10	10	10
20	10	10	9	10
22	10	10	9	10
24	7	9	9	9
26	6	9	9	9
28	5	9	9	9
30	5	9	8	8
32	3	9	8	3
34	3	8	5	3
36	3	8	1	3
38	3	7	0	1
40	3	6	0	0
44	3	6	0	0
46	2	6	0	0

Table 2. Number of larvae of three insect taxa surviving in four types of water in the second assay. Coefficients of variation for pH measurements (means shown) ranged from 3.0 to 5.3 %

Deleatidium spp.

	Clear water		Brown water	
Days	pH 7.7	pH 4.5	pH 7.6	pH 4.5
0	10	10	10	10
1	9	10	10	10
2	9	9	10	10
3	6	7	5	5
5	3	6	2	1
6	2	5	2	0
8	2	3	0	0
9	2	2	0	0
11	1	1	0	0
13	0	1	0	0
23	0	1	0	0
25	0	0	0	0

Olinga feredayi

	Clear water		Brown water	
Days	pH 7.7	pH 4.5	pH 7.6	pH 4.5
0	10	10	10	10
5	10	10	10	10
6	10	9	10	10
15	10	9	10	10
17	9	9	10	10
23	9	9	10	10
25	9	9	10	7
27	9	9	10	6
29	8	9	10	6
33	7	8	10	6
37	6	8	10	6
41	6	8	10	6
45	6	7	10	6
49	6	7	10	6
55	5	6	9	5
58	5	6	8	5
63	5	6	8	5
65	5	6	7	3
70	5	6	7	3
75	5	6	6	3
78	5	5	6	3
82	4	5	6	1
86	4	5	5	1

Austroperla cyrene

	Clear water		Brown water	
Days	pH 7.7	pH 4.5	pH 7.6	pH 4.5
0	10	10	10	10
8	10	10	10	10
9	10	9	10	10
19	10	9	10	10
21	10	9	9	10
49	10	9	9	10
55	10	9	8	8
58	10	9	8	7
63	10	9	8	7
65	10	8	7	7
70	10	7	7	7
75	10	7	6	7
78	10	6	6	6
82	10	6	6	6
86	10	5	6	5

APPENDIX VI

EFFECTS OF pH ON EPILITHON IN STEEP CREEK

INTRODUCTION

Experimental stream channels were used to determine the effects of elevated water pH on the development of epilithon in Steep Creek, an acid brownwater stream in South Westland (see Fig. 2.3.).

METHODS

Equipment and experimental set-up

Water from a pool behind a large debris jam in Steep Creek was diverted via a 6 cm diameter pipe through experimental channels located on the stream bank below. The bottom of the pool was lined with polythene sheeting to prevent water loss by seepage through the stream bed, and the ground beneath the channels was excavated to ensure that even during the lowest flows, there was always sufficient head of water to feed the channels. Water was passed first to a "header box" and, from there plastic hoses piped water to three channels (see Plate 7.1.). Each channel was 105 cm long, 7 cm wide and 6 cm deep, and was separated from adjacent channels by clear perspex dividers mounted on a plywood base coated with epoxy resin.

Two solutions of commercial grade KOH (0.5 and 1.0 M) were dripped into two channels at rates that increased water pH to about 6 and 7, respectively. Water in the third channel was not modified (pH about 4.5). Greywacke stones, stone chips on SEM stubs and carbon rods were placed in channels on 21 August 1985 and left there for 30 days. The pH of water in the channels was measured twice daily with a Metrohm E488 meter and water temperature was recorded daily. Water velocity in channels was estimated on eight occasions by determining the time taken for a twig to travel a known distance and adjusting for channel cross sectional area.

Analyses

SEM stubs with stone chips, stones and carbon rods were removed from channels on 20 September 1985. Stubs and rods were prepared for analysis as described in Section 7.2.1. Five randomly selected fields on stone chips from the three channels were examined (500 times mag.) and photographed using the scanning electron microscope to give a semi-quantitative assessment of periphyton density. The elemental composition of epilithic communities on carbon rods was determined by examining five randomly selected fields with EDAX using the peak identification option which measured the eight main elements present. Stones were taken back to the university on the day of removal in darkened jars containing cool water adjusted to the correct pH. TOC and photosynthetic pigment concentrations were measured on stones within two days by the methods described in Section 7.2.1. Recent work by Biggs (1987) indicates that chlorophyll degradation of epilithon should not have occurred in this time.

RESULTS

Experimental conditions

The pH of Steep Creek stream water (4.5 $\pm$ 0.2 (SD)) flowing through two artificial channels was elevated to 5.9 $\pm$ 0.6 and 7.2 $\pm$ 0.9, respectively by addition of KOH. Flows (~0.2 $l.s^{-1}$) and water temperatures (range during experiment = 5-11^{o}C) were the same in all three channels.

Epilithon biomass and structure

Very little epilithon developed on substrata in any channel over the 30 day period of the trial. Electron micrographs revealed that stone chip surfaces were covered lightly by inorganic particles and other amorphous material, and a few scattered diatoms (mostly *Fragilaria* spp.) were the only algae seen. Diatoms were most common (13 in five random fields (each 160 x 200 μm)) on stubs from the control channel whereas none were seen on stubs from the high pH channel.

Low epilithon biomass was confirmed by the negligible amounts of TOC (8.4-11.3 $\mu g.cm^{-2}$) and photosynthetic pigment (0.03-0.08 $\mu g.cm^{-2}$) recorded on any stones incubated in the channels (Fig. 1.). Mean concentrations of both declined with increasing channel pH, but only photosynthetic pigment concentration was significantly lower (ANOVA, P <

0.05). TOC concentrations were highly variable (CV = 53-64 %), probably because unequal amounts of fine particulate organic matter accumulated on the upper surfaces of stones which varied in degree of roundness.

Elemental composition

As in the stream (see Fig. 7.1.), silicon was the most abundant element followed by aluminium, iron and potassium (Fig. 2). Counts of the latter three elements declined significantly (Kruskall-Wallis, $P < 0.05$) with increasing channel pH. Silicon counts were lowest in the pH 7.2 channel where no diatoms were seen, and were highest in the pH 5.9 channel (Fig. 2.).

CONCLUSION

Because amounts of epilithon which accrued on artificial substrata after 30 days were very small, this experiment provided little information on the effects of pH on epilithon development. Nevertheless, algal colonisation did appear to be retarded when the pH of stream water was increased, suggesting that algae on stones in Steep Creek grew best in the naturally acid conditions.

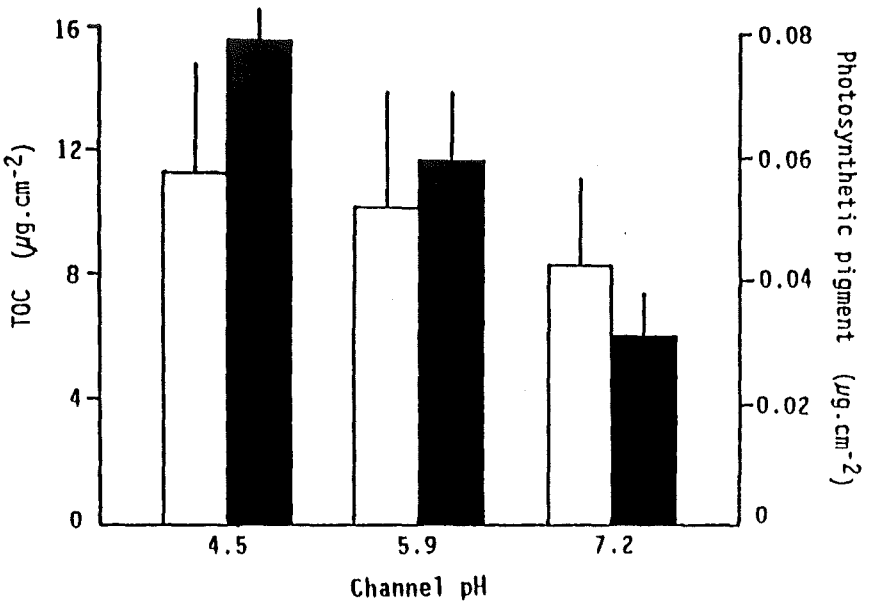

Figure 1. Total organic carbon (open bars) and photosynthetic pigment (closed bars) concentrations ($\bar{x}$ + 1 SE; n = 3) on stones kept at a mean pH of either 4.5, 5.9 or 7.2 for a month in three experimental channels at Steep Creek

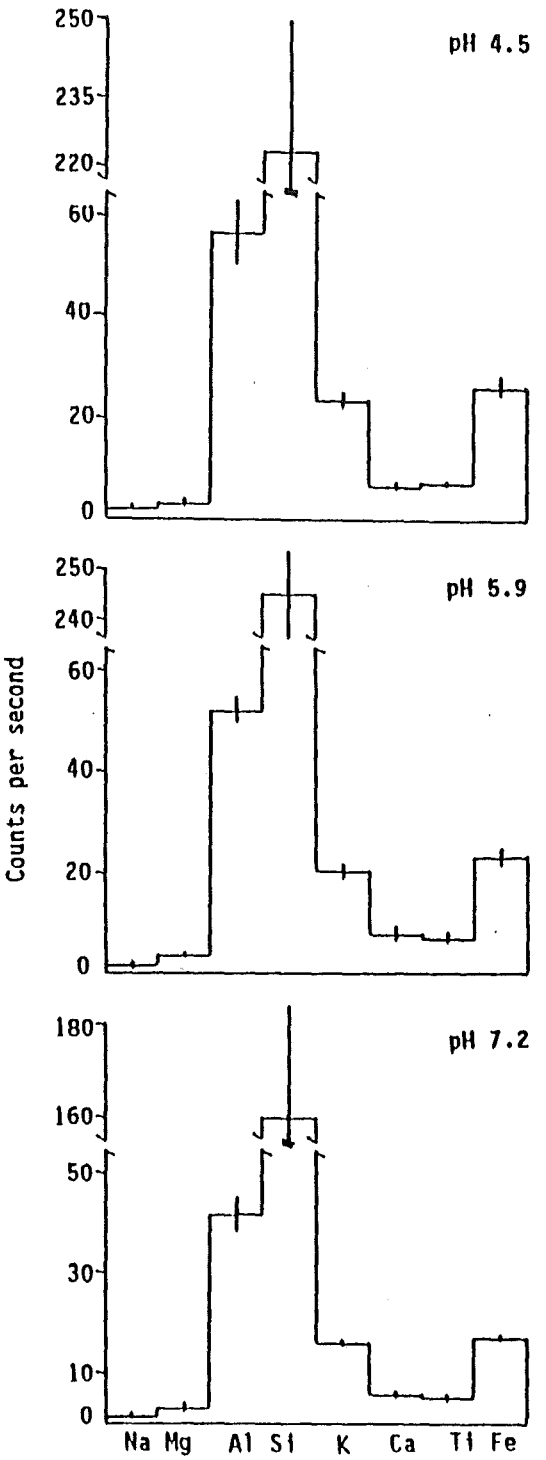

Figure 2. EDAX counts ($\bar{x} \pm 1$ SE; n = 5) of X-rays emitted by elements in epilithon (general fields) colonising carbon rods kept at a mean pH of either 4.5, 5.9 or 7.2 for a month in three experimental channels at Steep Creek.